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# **USSR Report**

**CHEMISTRY**

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ADSORPTION

UDC 541.138-183

ADSORPTION AND INHIBITORY EFFECTS OF THIAZOLE AND THIODIAZOLE DERIVATIVES:  
2-(p-AMINOBENZOSULFONAMIDE)-THIAZOLE ADSORPTION ON MERCURY ELECTRODE

Moscow ELEKTROKHIMIYA in Russian Vol 21, No 8, Aug 85  
(manuscript received 29 Jul 83) pp 1055-1059

LOSHKAREV, M. A., MICAL, N. N. and PILAVOV, Sh. G., Voroshilovgrad Agricultural Institute

[Abstract] Information available of the effects of various aliphatic and aromatic compounds on electroreduction of metal ions was expanded by experimental studies on the effects of adsorption of 2-(p-aminobenzosulfonamide)-thiazole (PABST) on a mercury electrode. The absorption isotherms and the electrical correlates in 2 N  $\text{Na}_2\text{SO}_4$ , 1 N  $\text{NH}_4\text{Cl} + 1 \text{ N NaCl}$ , and 3.75 N  $\text{NH}_4\text{Cl} + 0.325 \text{ N H}_3\text{BO}_3$  were evaluated in relation to zinc and cadmium reduction. There were both similarities and differences with the various solutions. In  $\text{Na}_2\text{SO}_4$  the value of  $\Gamma_{\text{ad}}$  was much greater than in the other solutions and approached  $3.32 \times 10^{-10}$  moles/cm<sup>2</sup>. Both replacement of  $\text{SO}_4^{2-}$  by  $\text{Cl}^-$  and of  $\text{Na}^+$  by  $\text{NH}_4^+$  led to a reduction in  $\Gamma_{\text{ad}}$ . Comparison of C vs. E plots for PABST, aniline and sulfanilic acid -- the latter 2 molecules used as representatives of different segments of PABST -- suggested that at positive potentials the presence of 2-aminothiazole fragment appeared to have no influence on PABST adsorption. At E = -0.6 v the PABST molecule appears to undergo a reorientation, and the decrease in adsorptive capacity after the reorientation peak (i.e., at more negative E values) is apparently due to orientation of PABST by the thiazole radical on the electrode surface. Figures 3; references 7: 4 Russian, 3 Western.

[046-12172/12955]

SURFACTANT CHARACTERISTICS OF POTASSIUM SALTS OF ALKYLMERCAPTOSUCCINIC AND ALKYLMERCAPTOPROPIONIC ACIDS IN AQUEOUS SOLUTIONS

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 8, 1985  
(manuscript received 20 Aug 83) pp 810-814

TANCHUK, Yu. V., Department of Petrochemistry, Institute of Physical Organic Chemistry and Coal Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A series of potassium salts of alkylmercaptosuccinic and alkylmercaptopropionic acids were studied for their surfactant behavior in aqueous solutions in relation to structure. Analysis of surface tension isotherms demonstrated that these salts do not differ qualitatively from other surfactants. In a given homologous series there prevailed a direct correlation between the length of the hydrophobic radical and the degree to which the surface tension was reduced at the water-air interface. With an increase in the concentration of one of these surfactants the surface tension falls to a plateau at a critical micelle-forming concentration for the given homolog. The minimum surface tension and the critical micelle-forming concentration of the surfactant are constant factors that are linearly dependent on the number of methylene groups in the hydrophobic radicals. The free energies for micelle formation are given for several surfactants, and shown to range from 7.45 to 15.50 kJ/mole. Figures 5; references 11: 9 Russian, 2 Western.

[045-12172/12955]

ADSORPTION OF DIRECT DYES ON ORGANOSUBSTITUTED MONTMORILLONITE

Ashkhabad IZVESTIYA AKADEMII NAUK TURKMENSKOY SSR: SERIYA FIZIKO-TEKHNICHESKIKH, KHIMICHESKIKH I GEOLOGICHESKIKH NAUK in Russian No 3, 1985  
(manuscript received 27 Jun 83) pp 105-108

SUBBOTINA, Ye. A., TARASEVICH, Yu. I. and ORAZMURADOV, A. O., Institute of Chemistry, TuSSR Academy of Sciences

[Abstract] Organosubstituted forms of Oglanlinskiy montmorillonite were investigated for their ability to adsorb unused dyes from waste water streams. Mineral samples were ground to pass through a 0.25 mm screen. They were then reacted with water solutions of N-cetylpyridine, a mix of quaternary salts of diethylaminomethylglycol esters of higher fatty acids ("alkamon OS-2"), tetramethylammonium chloride, and butylammonium chloride. Implanting in the interlayer spaces, these organic cations moved the structural elements of montmorillonite apart. X-ray diffraction measurements indicated the basal reflection of the untreated mineral was  $d_{001} = 1.24$  nm, typical for its sodium form. This increased to 1.32 nm when the butylammonium cation was introduced, 2.1 nm with the cetylpyridium cation, and 2.44 nm with the alkamon. With the cetylpyridium form, a sharp increase in the intensity of the

reflection indicated a highly ordered structure. Introduction of the cations gave the mineral a decidedly hydrophobic character, so the interlayer spaces tended to adsorb not water but the dye molecules in it. Adsorption trials were conducted with solutions of the dye direct yellow, with initial and final dye concentrations measured photometrically. The cetylpyridinium form of the mineral gave the best results, with basal reflection increasing slightly to 2.3 - 2.4 nm, indicating penetration of the dye molecules into the interlayer spaces. Low adsorption with the tetramethyl ammonium and butyl ammonium forms indicated only surface adsorption without such penetration into the interlayer spaces. OS-2 also gave good results, and with its relatively low cost, it is recommended as an effective long-chain modifier of montmorillonite for adsorbing dyes from water solutions. Figures 2; references 10: 7 Russian, 3 Western.  
[52-12672/12955]

UDC 678.544

#### ADSORPTION OF MOLYBDENUM BY CELLULOSE POLYPHOSPHATE FROM ACID SOLUTIONS

Minsk VESTNIK AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHMICHESKIKH NAUK in Russian No 4, 1985 (manuscript received 10 Dec 84) pp 54-57

LUNEVA, N. K., OPUTINA, A. G. and YERMOLENKO, I. N., Institute of General and Inorganic Chemistry, BSSR Academy of Sciences

[Abstract] Cellulose polyphosphate containing 5.0-11.0 mass % phosphorous was air dried and 1.5 g of it were put in a closed flask with 50 ml of ammonium molybdate solution (0.002-0.05 M) acidified with sulfuric acid to pH 1. With periodic mixing, equilibrium was reached in 2 h, the cellulose washed, dried and ignited in concentrated sulfuric acid with the addition of a small quantity of 30% hydrogen peroxide. The molybdenum content was determined by atomic absorption spectrometry. The higher the phosphorous content of the adsorbent, the higher the adsorption of molybdenum for solutions up to 0.02 M; above that increasing the concentration had no further effect. Varying the pH showed a maximum adsorption at pH = 2.6-4.5. Lowering pH to 0.8-2.6 showed lower total adsorption. Below pH = 0.8, adsorption rose again until, at pH 1, total adsorption was near maximum. Infrared spectroscopy indicated the formation of phosphoro-molybdenum structures in the polymer composition. Ultraviolet spectroscopy indicated that molybdenum interacts with the cellulose polyphosphate through chemisorption with the formation of molybdenum-containing structures with functional groups of the polymer. Overall, cellulose polyphosphate was shown to be an active adsorbent of molybdenum. Figures 3; references 8 (Russian).

[29-12672/12955]

ADSORPTION OF SELECTED DERIVATIVES OF POLYNUCLEAR AROMATIC HYDROCARBONS ON  
SILASORB 600

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHMICHESKAYA in Russian  
No 4, 1985 (manuscript received 4 Feb 84) pp 412-424

KOZLOVA, L. M., KLYAVINYA, Z. R., MEDNE, R. S. and SHATTS, V. D., Riga  
Polytechnic Institute imeni A. Ya. Pelshe; Institute of Organic Synthesis,  
Latvian SSR Academy of Sciences

[Abstract] In order to determine efficient chromatographic systems for the resolution of polynuclear aromatic hydrocarbons on silica, the chromatographic behavior of selected derivatives of naphthalene, anthracene and tetracene on Silasorb 600 was subjected to a quantitative analysis. The elution was conducted with hexane and combinations of hexane with more polar solvents, such as tetrahydrofuran, chloroform, or butyronitrile. Analysis of the retention times and adsorptivity parameters demonstrated that the compounds of interest showed only minimal displacement of the polar solvents from the surface of the silica gel bulk. Adsorption of the compounds to the gel surface involved both the carbon atoms and the polar fragments. On the whole, the various structural fragments had an essentially additive effect on adsorption, while intramolecular processes diminished retentivity 10<sup>3</sup>- to 10<sup>5</sup>-fold. The selectivity of tetrahydrofuran, chloroform and butyronitrile in the mobile phase can be utilized to assure resolution of selected combinations of compounds; furthermore, such polar solvents themselves can be used in optimal combinations. Figures 4; references 8: 2 Russian, 6 Western.  
[71-12172/12955]

## ANALYTICAL CHEMISTRY

UDC 543.4

### PHOTOMETRIC DETERMINATION OF TIN, ZIRCONIUM, NIOBIUM AND TANTALUM IN MARINE ALGAE

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 8, 1985  
(manuscript received 3 May 84) pp 857-859

VINAROVA, L. I., CHERNYSHEVA, M. A. and ANTONOVICH, V. P., Physical Chemical Institute, Ukrainian SSR Academy of Sciences, Odessa

[Abstract] The ash resulting from incineration at 700-800°C of the 'costal' red algae (Phyllophora) harvested in the Black Sea was analyzed for tin, zirconium, niobium and tantalum concentration by a photometric method. Determination of tin relied on the reaction of its complex with 3,5-dinitropyrocatechol with brilliant green, zirconium was determined from its color complex with arsenazo III, niobium was analyzed following its reaction with o-nitrophenylfluorone, and tantalum determinations relied on complex formation with salicylfluorone and ammonium oxalate. The order of magnitude of tin and zirconium (ca.  $1 \times 10^{-3}\%$ ) corresponded to the concentration of these elements in the Black Sea plankton. Niobium ( $1.7 \times 10^{-4}\%$ ) and tantalum ( $1.2 \times 10^{-4}\%$ ) were present in lower concentrations and the results represented the first determinations of this kind. References 6 (Russian).  
[045-12172/12955]

UDC 543.52:546.48

### RADIOCHEMICAL DETERMINATION OF SUBNANOGRAM QUANTITIES OF CADMIUM IN ENVIRONMENTAL SAMPLES

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 40, No 8, Aug 85  
(manuscript received 12 Jul 84) pp 1447-1455

SHAMAYEV, V. I. and TROITSKIY, D. A., Moscow Institute of Chemical Technology imeni D. I. Mendeleyev

[Abstract] A radiochemical interpolation method has been developed for the analysis of cadmium in environmental samples, which relies on the addition

of an interfering element, in this case zinc, in a 10- to 1000-fold excess. Three solutions -- the analyte and two standards with known zinc concentrations -- are extracted with dithizone and subjected to gamma-spectrometry. Using this approach, cadmium can be detected down to a concentration of ca.  $2 \times 10^{-10}$  M with acceptable selectivity. Combination of this approach with preliminary stoichiometric concentration improves the limit of detection to ca.  $2 \times 10^{-11}$  M cadmium and markedly enhances selectivity. This method has been found applicable to the analysis of a variety of environmental samples. Figures 6; references 9: 7 Russian, 2 Western.  
[048-12172/12955]

UDC 543.845+543.849

#### DETERMINATION OF SULFUR AND METALS IN ORGANIC COMPOUNDS

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 8, 1985  
(manuscript received 11 Jul 84) pp 854-857

OSADCHIY, V. D., Kiev Technologic Institute of Light Industry

[Abstract] A technique for the simultaneous determination of sulfur and metals (Fe, Co, Ni) in organic compounds has been devised which is based on pyrolytic decomposition of the sample at 900°C in a reducing atmosphere (heptane vapor). The volatile products are then passed through powdered chrome heated to 600°C, a step in which sulfur is converted to chromium sulfide while the metal remains as the ash residue. Subsequently both components were solubilized in concentrated hydrochloric acid, distilled water was added, and a soluble salt was formed from the metal. Since sulfur was analyzed on the basis of an equivalent concentration of chromium ions, loss of sulfur as hydrogen sulfide did not present a problem. Metal ion quantification is conducted on the basis of complex formation with EDTA. Trial runs with samples of nickel and iron salts of dimethyldithiocarbamic, sulfamic, and naphthionic acids and Urotropin-Co(II) sulfate yielded results with an absolute error of  $\pm 0.30\%$ , with a total time expenditure of 15 min or less per analysis. Figures 1; references 8 (Russian).  
[045-12172/12955]

UDC 543.4:543.7

#### PHOTOMETRIC DETERMINATION OF 3,5-DINITROBENZOIC ACID

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 40, No 8, Aug 85  
(manuscript received 9 Jul 84) pp 1515-1517

BARDIN, V. V., LEONTYEVA, L. B., MOKHOV, A. A. and PASECHNOVA, R. A.,  
Leningrad Technologic Institute imeni Lensoviet [Leningrad Soviet]

[Abstract] A simple method has been devised for the photometric analysis of 3,5-dinitrobenzoic acid (DNBA), using the high solubility of DNBA in

tetrahydrofuran (THF), ethanol and n- and isopropanol. Addition of NaOH to the DNBA solutions in the organic solvents of interest results in the formation of a colored substance absorbing at 400 nm, yielding a standard curve with a relative standard deviation of less than 0.004. The solubility of DNBA is too low in butanol for it to serve as a useful solvent in analysis. References 7: 5 Russian, 2 Western.  
[048-12172/12955]

UDC 543:546.562

#### ALLOY ANALYSIS ON BASIS OF COMPLEX FORMATION BETWEEN COPPER AND 14-MEMBERED TETRAAZAMACROCYCLICS

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 40, No 8, Aug 85  
(manuscript received 23 Jul 84) pp 1423-1426

PYATNITSKIY, I. V., NAZARENKO, A. Yu. and SICHKAR, N. Ye., Kiev State University imeni T. G. Shevchenko

[Abstract] Details are presented on a method of alloy analysis, utilizing the formation of complexes between copper and 14-membered tetraazamacrocyclic compounds. The method lends itself to photometric analysis of copper in a variety of substances, and also for the determination of aluminum and iron in copper alloys. Reaction of Cu with either 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (I) or rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (II) results in formation of complexes absorbing in the 510-520 nm range, yielding linear plots with Cu concentrations to 0.5 mg/ml. In view of the effectiveness of I and of II in binding Cu, this approach was also useful in the analysis of Al and Fe in copper alloys. With I, concentrations of Cu of 0.5-5% were detectable in the presence of excess Fe, Ni and Al. Copper complexes with II showed stronger absorption; however, selectivity vis-a-vis Ni, Co and Zn was significantly inferior to that obtained with I. Use of I as a masking reagent for Cu showed that it was superior to the use of thiourea and sodium thiosulfate as masking reagents in the determination of Al and Fe. References 14: 12 Russian, 2 Western.  
[048-12172/12955]

UDC 543.426

GAS PHASE ISOLATION AND SEPARATION OF TRACE ELEMENTS AS PREREQUISITE FOR ABSOLUTE ATOMIC FLUORESCENCE ANALYSIS

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 40, No 8, Aug 85  
(manuscript received 2 Jul 84) pp 1399-1406

RIGIN, V. I., Scientific Research and Design Institute for the Development of the Kansk-Achinsk Coal Basin, Krasnoyarsk

[Abstract] Theoretical considerations are presented for the use of preliminary atomization for the creation of a system of absolute atomic fluorescence analysis. The method has been found useful in the analysis of heavy metals, with the steps consisting of an initial extraction with bis-(trifluoroethyl) dithiocarbamate, subsequent gas chromatographic resolution of the volatile complexes, and final atomic fluorescence analysis. Analysis of Cd, Co, Cr and Cu samples provided by the National Bureau of Standards, USA, showed excellent agreement with results obtained by common conventional methods. References 39: 29 Russian, 10 Western.

[048-12172/12955]

UDC 542.61:543.38

EXTRACTION AND CHROMATOGRAPHIC ASSAY OF DICHLOROFOS

Kiev KHIMIYA I TEKHNOLOGIYA VODY in Russian Vol 7, No 4, Jul-Aug 85  
(manuscript received 27 Jun 84) pp 54-56

SHEVCHUK, I. A., DUBCHENKO, Yu. G. and NAYDENOV, T. S., Donetsk State University

[Abstract] Investigations were undertaken on the efficiency of several solvent systems for the extraction of dichlorofos from aqueous solutions, yielding extracts suitable for TLC and GLC analyses. Optimal extraction was obtained with 2:3 mixture of hexane:benzene, resulting in 62% dichlorofos recovery from a 7.12 g/liter solution, pH 6.5. Addition of 3.0 M aluminum nitrate to the dichlorofos solution improved recovery to 91%, while a repeat extraction raised the yield to 99.2%. The dichlorofos extracts obtained in this manner were suitable for analysis by TLC and GLC techniques, and increased the sensitivity of the latter analytical methods by an order of magnitude. References 8 (Russian).

[73-12172/12955]

BIOCHEMISTRY

UDC 541.49+541.67+541.69+546.04+547.962.7+546.732+546.742

STRUCTURAL FEATURES OF BIOMACROLIGANDS IN COMPLEX FORMATION WITH Ni(II)  
AND Co(II)

Kiev UKRAINSKIY KHMICHESKIY ZHURNAL in Russian Vol 51, No 8, 1985  
(manuscript received 23 Mar 84) pp 792-797

KOSTROMINA, N. A. and STRASHKO, V. V., Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Complex-formation between gliadins derived from different varieties of wheat with Ni(II) or Co(II) were monitored by nuclear magnetic proton relaxation spectroscopy in DMSO to provide data on the structural characteristics of gliadins. The presence of three (I, II, III) distinct regions on the relaxation plot was correlated with the disposition DMSO molecules on the gliadin molecule and within its cavities. The data corresponded to a U-shaped gliadin chain with binding sites within and without the U structure, and helical segments on the branches of this structure. Analysis of the Hill cooperativity coefficients for regions I, II and III for the binding of Ni(II) and Co(II) revealed marked differences between gliadins derived from high-, intermediate-, and low- quality wheats. Basically, the angle joining the two arms of the U structure in the high quality gliadins was much smaller than in the low quality gliadins, assuring a much more rigid molecular structure and firm complex formation. Gliadins derived from low-quality wheats were characterized by a much looser structure, the formation of weaker complexes, and distortion of the helical segments. Figures 3; references 12: 6 Russian, 6 Western.  
[045-12172/12955]

UDC 535.371+577.164.12

STUDY OF RIBOFLAVINE FLUORESCENCE QUENCHING BY NICKEL, COPPER AND ZINC  
HISTIDINATES AND ALANINATES

Kiev TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA in Russian Vol 21, No 4,  
1985 (manuscript received 30 Jul 84) pp 488-493

LUGINA, L. N., DAVIDENKO, N. K. and GAVRISH, S. P., Institute of Physical  
Chemistry imeni L. V. Pisarzhevskiy, UkrSSR Academy of Sciences, Kiev

[Abstract] The goal of this study was to investigate the quenching of riboflavin (RF) fluorescence in solutions containing aminoacids alanine and histidine and  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions. The quenching of RF fluorescence may be caused by a number of reasons: energy transfer from an excited flavine molecule to the quencher (free metal ion or its complex), by formation of reduced, nonfluorescent flavine or by formation of nonfluorescent double or triple complexes. The data obtained in this study showed that quenching of RF fluorescence is primarily due to nonradiating transfer of energy from the donor (RF) to metal ions. The formation of unstable, nonfluorescent histidine complexes could also contribute to the fluorescence quenching. Finally, free histidine and Zn-histidinates quench RF fluorescence by electron transfer to the excited flavine molecule, leading to the formation of reduced, nonfluorescent RF. RF appeared not to be forming any complexes with Ni, Zn or Cu admixtures. Figures 4; references 9: 4 Russian (1 by Western author), 5 Western.

[53-7813/12955]

UDC 547.587.52.04.535.37

SYNTHESIS OF *o*-ACYLMINO DERIVATIVES OF 4-METHYL-7-HYDROXYCUMARINE  
(4-METHYL-UMBELLIFERONE)

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian Vol 217, No 7, Jul 85  
(manuscript received 25 Jul 84, after revision 6 Nov 84) pp 906-909

KOZLOVA, I. K., Institute of Biological and Medical Chemistry, USSR Academy  
of Medical Sciences, Moscow

[Abstract] The article reports on synthesis of 6- and 8-N-hexadecanoylamino-4-methylumbelliferone, aglycones of corresponding glycosides used as fluorogenic substrates for determining activity of glycocerebrosidases, as well as in diagnosis of certain hereditary ailments related to enzyme deficiencies. Special emphasis is placed on the synthesis of fluorogenic aglycones and their physico-chemical properties. The initial compound was 4-methyl-umbelliferone, which was selectively nitrated to produce either the 6- or the 8-nitro-isomer, with expectation that the former would predominate. Results showed that nitration of 4-methyl-umbelliferone with tetrafluoroborate of nitronium in acetonitrile produced 65% of the 6-nitro-isomer; its reduction

to the 6-amino-derivative of o-aminohydroxycumarines also produced good yields. The compounds were fluorinated with augmentation as the solutions were alkalized to pH of 10-11. The magnitude of quantum yield was determined by the position of the acylamide group on the pyrone ring. The 6-N-hexadecanoylamino-4-methylumbelliferon had markedly better fluorogenic qualities and is to be preferred for synthesis of fluorogenic substrates. Data on synthesis and PMR spectra are summarized in an experimental section. References 9: 1 Russian, 8 Western.  
[40-12131/12955]

UDC 547.466:577.15.08

#### ENZYME SUBSTRATES. PART 3. SYNTHESIS OF N-HIPPURYL-L-PHENYLALANINE

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHMICHESKAYA in Russian No 4, 1985 (manuscript received 20 Dec 84) pp 485-488

ZITSANE, D. R., RAVINYA, I. T., TETERE, Z. F., STRAKOVA, I. A., RIYKURE, I. A. and GUDRINIYETSE, E. Yu., Riga Polytechnic Institute imeni A. Ya. Pelshe

[Abstract] In order to provide an efficient method of synthesis of N-hippuryl-L-phenylalanine (I), a synthetic substrate used in the determination of carboxypeptidase A activity, studies were conducted on the reaction of cyanomethyl and pentachlorophenyl esters of hippuric acid with methyl L-phenylalanine HCl. Superior yields (90%) were obtained in reactions involving the hippuric esters and the methyl L-phenylalanine in a tetrahydrofuran solvent system supplemented by catalytic quantities of glacial acetic acid. The yield was in general higher with the use of cyanomethyl hippurate. References 20: 1 Hungarian, 7 Russian, 12 Western.  
[71-12172/12955]

CATALYSIS

UDC 541.128.13

ACTIVITY OF IRON-COBALT CATALYSTS IN AMMONIA SYNTHESIS AND THEIR STRUCTURAL CHARACTERISTICS BASED ON -RESONANCE SPECTROSCOPY DATA

Kiev TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA in Russian Vol 21, No 4, 1985 (manuscript received 24 Sep 84) pp 500-504

YATSIMIRSKIY, V. K., ISHCHENKO, Ye. V., MAKSIMOV, Yu. V., ARENTS, R. A. and SUZDALEV, I. P., Kiev University

[Abstract] Structural characteristics of ion-cobalt ammonium catalysts formed in a stream of H and N were investigated by the method of Mossbauer spectroscopy, comparing the catalytic properties with their specific structures. An interesting phenomenon of microlamination of iron-cobalt alloys was observed in the range of 14-18% Co. The most reactive samples in synthesis of ammonia were those with microheterogenic alloys. The appearance of microheterogeneity was related to the specificity of the formation of these catalysts. Figures 3; references 12: 10 Russian, 2 Western.  
[53-7813/12955]

UDC[66.023:66.097.322].004.2

PARAMETRIC SENSITIVITY AND PRODUCTIVITY OF TUBULAR REACTOR

Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 8, 1985 pp 454-458

EVENCHIK, A. S., MAKHLIN, V. A. and SLINKO, M. G.

[Abstract] Cooled tubular reactors with immobile catalyst are widely used in exothermic catalytic processes. However, one of their characteristic properties is the so called runaway, which could occur under some conditions just after a slight temperature change. The goal of this study was to review the areas of stable exploitation of tubular reactors with internal cooling system. A theoretical discussion of the runaway conditions is presented based on a quasihomogeneous diffusion model. Determination of the conditions of a runaway in tubular reactors resembles the phenomenon of heat blast in a vessel with conductive heat removal to the walls of such a vessel. Several

variants of possible scenarios (air and oxygen processes) are discussed. To exclude the possibility of local blasts, the following conditions are necessary: careful purification and packing of the catalyst, the use of non-tarring heat carrier, avoidance of addition of the catalyst during the on-going process, strict temperature control and, possibly, conversion from circulating to boiling heat carrier. Figures 3; references 25: 6 Russian, 19 Western.

[61-7813/12955]

UDC 541.128.13

#### MECHANISM OF ACTION OF ALKALINEPROMOTERS IN CATALYSTS FOR SYNTHESIS OF AMMONIA

Kiev DOKLADY AKADEMII NAUK UKRAINSKOY SSR: SERIYA B in Russian No 9, Sep 85  
(manuscript received 19 Mar 85) pp 50-53

SAMCHENKO, N. P. and GOLODETS, G. I., Institute of Physical Chemistry UkrSSR  
Academy of Sciences, Kiev

[Abstract] An attempt was made to elucidate the mechanism of action of alkaline promoters at the stage of reduction of an iron catalyst used in synthesis of ammonia, when their porous structure, surface area and capacity for dispersion are formed. The factors determining these characteristics are: temperature and rate of reduction as well as the speed of the removal of steam formed during the reaction. Experimental results showed that an increase in steam concentration ( $\text{CH}_2\text{O}$ ) leads to larger size of iron crystals. The  $\text{CH}_2\text{O}$  could be varied by changing the composition of promoters affecting the rate of reduction. Increased size of the crystal in presence of  $\text{K}_2\text{O}$  and their decrease in presence of  $\text{Al}_2\text{O}_3$  makes it possible to select a combination of  $\text{Al}_2\text{O}_3 + \text{K}_2\text{O}$  which assured formation of medium size Fe crystals with optimum values of  $q_{\text{N}_2}$ , assuring an average cover of the surface with nitrogen and maximum rate of the synthesis of ammonia. This is the main role of promoters in catalysts used in synthesis of ammonia. Figures 3; references 8: 6 Russian, 2 Western (1 by Russian author).

[86-7813/12955]

IDENTIFICATION OF POTENTIAL GENERATING PROCESSES ON Pd AND Pt CATALYSTS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 284, No 5, 1985  
(manuscript received 18 Dec 84) pp 1155-1157

BIZHANOV, F. B., SOKOLSKIY, D. V., academician, Kazakh SSR Academy of Sciences, and DINASYLOVA, Sh.D., Institute of Organic Catalysis and Electrochemistry, Kazakh SSR Academy of Sciences, Alma-Ata

[Abstract] A computer program written in FORTRAN was used to determine the relationship between measured potentials on Pd and Pt hydrogenation catalysts and hydrogen pressure, temperature, and the metal used in 0.1 N  $H_2SO_4$ . The fundamental approach relied on the analysis of the  $E-t$  relationship expressed by the first order aperiodic equation  $E(t) = K(1 - e^{-K_1 t})$ , where  $E$  = catalyst potential at time  $t$ , and  $K$  and  $K_1$  are coefficient encompassing additional coefficients for temperature and pressure. The derived expression were found to give good correlation (5%) with experimentally measured results for 5% Pd/C and 5% Pt/C. Thus, the proposed program can be used for the estimation of catalyst potential at any given moment of time, and for an estimate of the time required for an equilibrium hydrogen potential under defined temperature and hydrogen pressure. Figures 2; references 6 (Russian).  
[99-12172/12955]

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CATALYTIC ACTIVITIES OF OXIDIZED CHARCOALS IN HYDROLYTIC REACTIONS:  
RELATIONSHIP BETWEEN HOMOGENOUS AND HETEROGENOUS CATALYSTS

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 14 Dec 83) pp 864-869

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[Abstract] Studies were conducted on the kinetics and activation parameters of oxidized charcoal- and carbon black DG-100-catalyzed hydrolysis of ethyl acetate and sucrose inversion. The 23 samples of oxidized charcoal were prepared by treating activated charcoal derived from phenol-formaldehyde resins with air,  $HNO_3$ ,  $H_2O_2$  or  $NaClO$ . Analysis of the data obtained with the oxidized charcoals and comparison with similar data for reactions catalyzed by sulfonated cation exchangers (KU series) and  $HCl$  demonstrated a common mechanism regardless of the catalyst. The key factor promoting catalysts was 'effective acidity'. The latter concept represents an additive function of three types of charcoal acidity, predicted on the nature of the surface protonogenic groups ( $h$ ), their concentration per surface area ( $S$ ), and pore volume ( $P$ ). Mathematical equations were derived for the estimation of  $h$ ,  $S$  and  $P$  for the different types of oxidized charcoals. Figures 2; references 14: 13 Russian. 1 Western.

[75-12172/12955]

EFFECTS OF POROUS STRUCTURE OF PROMOTED Zn-Cr CATALYST ON EFFICIENCY AND SELECTIVITY OF COMBINED SYNTHESIS OF METHANOL AND HIGHER ALCOHOLS FROM CO AND H<sub>2</sub>

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 9 Mar 83) pp 870-878

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[Abstract] Zn-Cr catalysts used for the joint synthesis of methanol and higher alcohols from CO and H<sub>2</sub> under a pressure of 24.5 MPa at 300-420°C were assessed for the effects of their porous nature on the efficiency and selectivity of the process. The catalysts, prepared under pressures ranging from 264 to 1056 MPa, were characterized by similarity in micropore radii, but differed in the volumes and radii of their meso- and macropores. The macrostructural differences were found to exercise a profound effect on catalytic efficiency and selectivity, with different catalysts showing maximal selectivity for methanol and the higher alcohols. In the latter case, catalysts with greater selectivity also showed greater thermal stability. An increase in the concentration of CO<sub>2</sub> depressed selectivity for the higher alcohols, while an increase in the partial pressure of CO (with H<sub>2</sub>/CO = 2.7 or less) improved such selectivity. However, in the latter case the efficiency of CO conversion to the higher alcohols decreased due to greater formation of CO<sub>2</sub> and CH<sub>4</sub>. Figures 3; references 9 (Russian).

[75-12172/12955]

BUTANE OXIDATION: EFFECTS OF V:P RATIO ON CATALYTIC CHARACTERISTICS OF V-P-O CATALYSTS

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 18 May 84) pp 885-891

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[Abstract] An analysis was conducted on the effects of the V:P ratio in V-P-O catalysts on the catalysis of butane oxidation. The studies were conducted at 763-823°K, using catalysts with V:P ratios ranging from 1:0.50 to 1:3.24. Optimal yield of maleic anhydride was obtained with catalysts for which the V:P ratio was ca. 1:1, with catalysts with a V:P > 2.5 showing virtually no activity. Thus, the addition of nonstoichiometric P increased the activity of the V-P-O catalysts and the rate of formation of partial

oxidation products. Synthesis of catalysts with excess phosphorus is possible via intermediate formation of the alpha- $\text{VOPO}_4$  phase. Other methods of introducing excess P lead to the formation of the low-activity metaphosphates  $\text{VO}(\text{PO}_3)_2$  and  $\text{V}(\text{PO}_3)_3$ . Figures 4; references 15: 8 Russian, 7 Western. [75-12172/12955]

UDC 541.124:542.973.7:546.262.31:546.98'655'623:543.422.27

#### REACTIVITY OF $\text{O}_2^-$ AND MECHANISM OF LOW-TEMPERATURE OXIDATION OF CO OVER $\text{Ce}/\text{Al}_2\text{O}_3$ AND $\text{Ce-Pd}/\text{Al}_2\text{O}_3$

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 14 Feb 84) pp 924-931

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[Abstract] An ESR study was conducted to determine whether  $\text{O}_2^-$  radicals are formed on the surface of  $\text{Ce}/\text{Al}_2\text{O}_3$  (I) and  $\text{Ce-Pd}/\text{Al}_2\text{O}_3$  (III) catalysts, and to assess their behavior in oxidation of CO at low temperatures. The studies conducted at 343-448°K demonstrated that such anion radicals are formed, and that the rate of reaction of  $\text{O}_2^-$  with CO and  $\text{C}_2\text{H}_4$  over II was one- to two-orders of magnitude greater than over I. The presence of Pd in the catalysts increased the heterogeneity of the  $\text{O}_2^-$  species formed and promoted the genesis of more active  $\text{O}_2^-$  radicals. The addition of Pd to a concentration of 0.1 and 0.5% reduced the energy of activation of the more active  $\text{O}_2^-$  radicals from 40 to, respectively, 33 and 31 kJ/mole. Figures 4; references 11, 7 Russian, 4 Western. [75-12172/12955]

UDC 542.973:546.562:541.641+66.095/.097

#### IMMOBILIZED CATALYSTS. PART 14. EFFECTS OF SYNTHETIC CONDITIONS ON FIXATION OF $\text{Cu}(\text{II})$ COMPLEXES

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 18 Jul 84) pp 945-952

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[Abstract] Chemical analysis, IR spectroscopy and radioisotope technology were employed in an assessment of the mechanism of fixation of  $\text{Cu}(\text{OCOCH}_3)_2$  to polyethylene-poly(acrylate) (PEPA) and of the structure of the immobilized  $\text{Cu}(\text{II})$  complexes. Studies over the temperature range of 333 to 949°K provided

Langmuir plots that yielded a stability constant for the Cu(II) complexes equal to 300 liters/mole at 333°K. Maximum binding of Cu(II) corresponded to 0.35 moles/mole, equivalent to 22.22 mg Cu(II)/g PEPA. The degree of Cu(II) binding is highly temperature dependent, increasing sharply at temperatures above 333°K. With an increase in the reaction temperature from 333 to 363°K the concentration of unreacted carboxyl groups decreased from 44 to 17 mole% in the presence of equimolar concentrations of reactants. The stepwise binding mechanism involved initially one grafted carboxyl group (approaching 16 mole% of bound Cu(II) ( $k_1 = 1.6 \times 10^{-3}$  moles/g), and then a second carboxyl group ( $k_2 = 2.54 \times 10^{-3}$  moles/g). Figures 4; references 12: 6 Russian, 6 Western.  
[75-12172/12955]

UDC 541.128.12:542.924.4:547.292'214:54-39:546.712/713

#### NOVEL CATALYTIC REACTION OF CO WITH H<sub>2</sub>

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 10 Jan 85) pp 1018-1019

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[Abstract] An analysis was conducted on the reaction products obtained by the reaction of CO with H<sub>2</sub> over Fe catalyst, with the reactant mixture containing low concentrations of phenylacetylene. From reactions carried out at 130-165°C under pressures of 25-100 atm and CO:H<sub>2</sub> = 2:1 to 1:2, a homologous series of aromatic alcohols was synthesized. The products were identified as 3-phenylpropanol-1 and its homologs, largely in the n-conformation, containing 4 to 8 C atoms in the side chain. References 3 (Russian).  
[75-12172/12955]

CHEMICAL INDUSTRY

ADVANCES IN AMMONIA PRODUCTION TECHNOLOGY

Moscow SECOND PROGRAM "MAYAK" in Russian 1530 GMT 24 Oct 85

[Summary] The All-Union Scientific Research and Design Institute of Chemical Engineering has developed new technology in ammonia production. The Institute's chief designer, Krotov, described the new line, saying that it will "greatly reduce consumption of both energy and metal in the manufacture of equipment."

The technology incorporates fundamentally new equipment at almost every stage of ammonia production, including mass exchange equipment for purifying carbon gas. Prototypes of this equipment have been tested at Tolyatti Azot, [Association], demonstrating the possibility of reducing metal consumption in the equipment's manufacture by nearly half. Ammonia production will approach 475,000 tons per year.

In the next five-year plan, several such lines will be introduced. The "tandem" system holds out hope of an even more economical method, since it will use heat generated during the production process itself in the manufacture of ammonia.

/12955  
CSO: 1841-87-P

CONFERENCE ON INDUSTRIAL USE OF CHARGED-PARTICLE ACCELERATORS

Leningrad LENINGRADSKAYA PRAVDA in Russian 23 Oct 85 p 2

[Text] Beams of elementary particles accelerated to tremendous speeds and energies in accelerators have been put to work in metallurgy and in the textile and chemical industries. New applications of radiation technologies are being discussed at the Fifth All-Union Conference on the Employment of Charged-Particle Accelerators in the Economy, which opened yesterday at the House of Friendship and Peace with Peoples of Foreign Countries. Taking part in this conference, together with Soviet engineers and scientists, are specialists of Bulgaria, Hungary, the German Democratic Republic, Poland and Czechoslovakia.

"In a comparatively brief period of time, accelerator technology has earned deserved recognition in the most diverse branches of our country's industry and in agriculture and medicine," said A. A. Vasilyev, head of an administration of the USSR State Committee on the Use of Atomic Energy, opening the conference. "The use of accelerators in industrial radiation-technology units has made it possible to put into production a number of products and materials with qualitatively new properties, to increase labor productivity substantially, to reduce pollution of the environment and to lower energy consumption."

Representatives of more than 100 organizations who are taking part in the conference are exchanging experience development of new types and modifications of accelerators, and they are discussing problems connected with the development of new-generation equipment and the introduction of revolutionary processes on a large scale.

FTD/SNAP  
/12955  
CSO: 1841/142

## STRATEGY OF BIG CHEMISTRY

Moscow ZNANIYE-SILA in Russian Vol 698, No 8, 1985, inside front cover - p 2

[Article by V. Shelepin]

[Text] Acceleration of scientific-technical progress is a vital necessity. This means a transition to fundamentally new production systems, and not improvement of existing machinery and procedures. The scientific-technical revolution is characterized by a qualitative jump in engineering and technology. Surmounting obstacles in the path of introducing the accomplishments of science into production is an urgent problem.

### One Product--450 Developments

Until recently there was a certain "watershed" separating chemistry, one of the principal natural sciences, from chemical technology, an applied science. The two developed independently, and only in the final stage did they merge into a single flow. Now chemistry is both science and production. Although the distance from fundamental chemical research to its embodiment in a multiton installation is sometimes extremely great.

Intensification of chemical production operations is proceeding in many directions, but the chief ones are improving existing production procedures and introducing new ones, increasing the unit output capacities of chemical production operations, developing new sources of raw materials, and combining chemical production operations. And finally there is the transition from automation of individual production processes to full automation of production operations.

Our country's chemical production volume increased by a factor of 2.3 in the last 10 years. But consumption of electric energy grew by only a factor of 1.7, while consumption of thermal energy grew by a little less than a factor of 2. These are the direct consequences of intensification, which necessarily foresees such sensible utilization of different forms of energy.

On the average labor productivity in chemical industry is 20-25 percent higher than in other sectors. But what is most important is that chemicalization is raising labor productivity in all production operations--both those directly associated with chemistry and those utilizing its products and intermediate

products. That is, chemicalization quickly leads to intensification in associated sectors and even in sectors quite distant from chemistry.

This is precisely why there are advantages to developing chemical industry at an accelerated rate. And in fact, while in the 1950s total world production tripled, it increased in chemistry by a factor of 20. Three and twenty! Now that is persuasive!

Unfortunately even countries possessing highly developed chemical industry typified by rich traditions are frequently unable to achieve economic and technical indicators that are fully in keeping with the present level of chemical science and with the society's needs. The problem is that large enterprises--they make the main contribution to production of a given form of products--are extremely capital- and metal-intensive objects. Their reconstruction and reequipment are so complex that it is often more advantageous to build a new production operation than to adapt an old one.

From the standpoint of the chemical process engineer, the intensity of a chemical process depends on selecting the operating conditions or mode of production equipment which would not only cause the chemical reaction to proceed at a maximum rate but which would also maximize the product yield. It is with this purpose in mind that we try to maintain the best temperature conditions in the reaction zone, and the necessary concentration of products, pressure, heat withdrawal or input, and the like. This means that preliminary scientific studies are required. And in fact, twice more assets are spent on chemical research in developed countries than on research in other sciences. Twenty percent of the world fund of patents has been issued for inventions in chemistry.

And in the not-too-distant past, a single chemical product introduced into production required 450 theoretical developments, 97 laboratory studies and 8 attempts at experimental production.

But the resulting effect usually exceeds all of these outlays by many times. Renovation of the product assortment of chemical plants is now proceeding at an average of every 10 years. Half of the products produced today were completely unknown two decades ago.

Solution of the raw material problem, which is troubling mankind more and more, also rests on the shoulders of chemistry. Complete wasteless utilization of minerals is based chiefly on competent utilization of chemical processes. Wasteless production is essentially the highest level of intensification of a process. After all, this means complete elimination of the extra outlays of labor associated with preparing, removing, transporting, storing or burying wastes. If there are no wastes, there are no extra labor outlays. Concurrently profitability rises because former wastes become valuable goods, and this reflects itself favorably in the economic indicators. Both the individual enterprise and society as a whole win out. The urgency of economical expenditure of resources has recently grown even more. This has been noted in various party and state documents.

Here is but one example. An active effort is being made today in all places to replace metallic piping by plastic piping made from polyvinyl chloride and polyethylene. The country needs about 15 million tons of polymer piping per year. At this level of production, 10 million tons of oil are saved each year. Where does this savings come from? The fact is that 4 times less thermal and electrical energy is required to make plastic than the amount required to make the same quantity of steel. When polymers replace nonferrous metals, the payoff is even greater, and the energy outlays decrease by a factor of 5-6.

But what is even more important is that use of polymers and plastics, and substitution of traditional metals by them, raises labor productivity in the processing sectors of industry. That is, all sectors of the economy that make some kind of use out of these materials benefit.

And therefore introduction of polymers is continually widening. At first there were 34 kilograms of plastic parts in the Zhiguli automobile, while in new models there are over 70 kilograms of such parts, and in future models there will be over 90 kilograms.

Academician N. M. Zhavoronkov once noted the following: "The research chemist learns new things, while the chemical process engineer creates new things." Of course, even though there is a certain division of labor here, the objective of the two is the same. But the present stage is doubtlessly unique in that the process engineer, who is the leading figure in the "creation" stage, has now obtained significant rights in the "learning" stage.

#### How to Get Away from the Test Tube

In modern devices used for major chemical processes, much depends directly upon chemical, physical, thermodynamic and even geometric factors. The reason that many factors are involved in the chemical production process is that it not only yields to analysis with difficulty (even with the most modern methods), but it also is simply difficult to understand. Hence follow significant difficulties in the transition from the laboratory to industrial installations. This is the so-called problem of transition of scale. It is one of the principal problems in chemical technology. It was found to be an extremely great obstacle in the 1920s, when heterogeneous catalytic reactions were introduced and when the productivity of industrial installations increased dramatically.

The path taken in solving the problem was purely empirical, and it consisted of many stages. Following laboratory work, a so-called pilot unit was built, one resembling an industrial unit only in the first approximation. This was followed by creation of equipment for experimental production, for semi-industrial production, and only in the last stage for industrial production. Ammonia synthesis is a good example. In this case empirical improvements in the production operation went on from 1911 to a minimum of 1965--over 50 years!

Gradually the problem of the transition of scale began to be solved more successfully, which is very graphically illustrated by growth in the relative productivity of the production units. In 15-20 years the dimensions of the

main production units of chemical production operations grew by a factor of 5-10. In the mid-1950s an installation that produced 50,000 tons of ethylene per year was said to be very large; in the 1970s productivity was raised to 200,000 tons per year, which incidentally reduced product cost by 40 percent. Today, plans for production units with output capacities of up to a million tons of ethylene per year are being discussed. This is an increase of 20 times!

The desire to maximally increase the relative output capacity of a production unit can be explained in a number of ways. First of all the relative capital investments (per unit of productivity) decrease. For example a fourfold increase in the productivity of an ethylene production operation requires but a 2.5-time increase in capital investments.

Second, as a rule the relative productivity of the production units (per unit time) increases. The dimensions of ammonia reactors quadrupled in the last 15 years, while their relative productivity rose by a factor of 15. It is believed that the tendency toward intensification of the discharge of products per unit reactor volume will persist into the foreseeable future.

The dimensions we are talking about are those of chemical installations--columns, converters, reactors, furnaces. What are they like today? In the middle of our century, designers achieved full utilization of the dimensions that rail transportation would allow. This meant that the diameter of apparatus had to be limited to 3 meters. But the length of apparatus assembled at plants attained 30-50 meters. For a long period of time the 3 meters were a unique psychological barrier that few dared to cross.

Then the interests of intensification became dominant over the desire to complete manufacture of an apparatus in a plant shop. Apparatus with a diameter of up to 10 meters began to be erected right at the construction sites. For example, contact furnaces for production of sulfuric acid having a 5 meter diameter are now routinely encountered.

Nonetheless assembly of giant apparatus at construction sites did not achieve full acceptance. It is still more advantageous to complete the manufacturing cycle at the plant. What is the solution to the problem? We need to create special transportation resources by which to deliver equipment via highways and waterways. Multiwheeled tired trucks with individual hydraulic or electric motor drives for each wheel can transport equipment weighing up to 8,000 tons. This is more likely an optimum, though not in terms of the conditions of the chemical production operations but rather in terms of the possibilities of delivering the apparatus at an acceptable transportation cost. And when the plant and the future chemical enterprise are located on the shore of a waterway, there are no restrictions on the dimensions and weight of the equipment.

#### A Ship-Building Dock Builds a Chemical Plant

Construction of large plants at plants--predominantly at ship-building docks--is the present trend. Ship-building industry has undergone fundamental change of graphical proportions. Besides launching vessels into the water, it is

now creating ready-to-operate chemical plants with maximum possible productivity and, consequently, effectiveness. "A Plant Is Created at Plants": Such a title of an article journal may not be very original, but it represents a stage in the machine building practice of leading countries that has already been assimilated.

But we will not get carried away with this approach. The effectiveness of superproductive installations still does leave something to be desired.

For example, it has rarely been possible for anyone to achieve productivity that is at least 60-80 percent of expected productivity in the first 2 or 3 years. There are both traditional problems of the transition of scale, and there are purely organizational and technical problems. It must not be forgotten that the period of obsolescence of production processes is not very long today. Moreover the effort it takes to keep giant installations operating normally cannot even be compared with similar measures involving devices of moderate productivity. Everything in the former case is much more complex. Given a standard work time of 8,400 hours, it is difficult to achieve even 8,000 hours of continuous work per year. Consequently creation of production units characterized by the maximum possible relative productivity is a two-sided problem. Technically it is possible. But is it economically feasible?

At the moment this question cannot be answered unambiguously.

#### What, Where, When and How

Mention should be made here of the bank of raw data necessary for designing a new giant production operation. No chemical process can do without meticulous control--without measurement of different parameters. But what is to be measured? This question might appear naive at first glance. But alas, it is far from an idle one. It would be simply impossible to introduce new substances into production without preliminary meticulous study of their chemical and thermodynamic properties. Only in this case can the process engineer determine what, where, when and how to measure.

A stable flow of quantitative data on the properties of substances is required. Development of industry step by step on the basis of gradual empirical improvement of procedures is unacceptable, because it is too expensive. Any modernization of production must be preceded by fundamental research on the behavior of substances in conceivable and inconceivable experimental and industrial conditions. The situation is complicated by the fact that mixtures and not pure substances are used more often in practice. Experimental study of the properties of mixtures is noticeably more complex. This is why we need to hasten development of thermodynamic methods of building models of the behavior of substances. The models must be based on experimental data for pure substances and for mixtures, obtained in limited intervals of temperatures, pressures and compositions.

It should be noted that the data precision requirements are growing from year to year. Unfortunately such high precision requirements are not always received approvingly. However, science knows of many examples in which what

appeared to be an "unnecessary" degree of accuracy led to a previously unpredictable success. For example the densities of different grades of nitrogen were once measured with a precision that was totally unnecessary at that time--0.1 percent. But as a result argon was discovered, to become in the final analysis the basis for development of the corresponding sector of industry. The periodic law would not have been discovered by Mendeleev, had there not been sufficient quantitative data on the atomic and molecular characteristics of matter.

The struggle against pollution of the air and water basins is being hindered to a considerable degree by the absence of the most important information on the influence of wastes and exhausts on the environment at the moment many chemical production operations are started up. This is why quantitative analysis and comprehensive information on the properties and behavior of matter have decisive significance to intensifying chemical production operations and making them ecologically harmless.

#### Not a Sum, But a Complex

Traditionally, small, medium-sized and very large chemical enterprises have been designed as a certain sum of relatively independent facilities. These independent facilities included, as an example, the steam supply system (steam boilers of different types and productivities), the water preparation system, the waste treatment or utilization system, and the chemical production operation per se.

It is obvious to any process engineer that for practical purposes each complex may be represented as the sum of three mutually related components, irrespective of the specific production process. First there are the chemical processes, including those which proceed together with liberation or absorption of heat or other forms of energy. The second is the thermal energy regeneration and utilization system. And third and finally, there is the energy supply system providing electricity, water vapor of different pressures or other sources of energy (emissions).

Despite the simplicity of this division, it does reflect the general picture with sufficient accuracy, and it may be laid at the basis of mathematical models for optimizing practically any chemical production operation.

Mathematical modeling is the most important stage of solving the problems of transition of scale. Successes in computer technology and applied mathematics have dramatically altered the approach to designing chemical machine units. In this case the real process is studied successively at several levels: the atom, the molecule, the microregion, the reactor element, the reactor, the installation. All of this produces an accurate and detailed picture.

These methods are so well developed today that a possibility has appeared for assimilating the next step--progressing to construction of mathematical models of a chemical production operation as a whole. Such a model must embrace all of the components of the complex irrespective of their purpose. Their aim must be to minimize energy consumption, minimize the number of pieces and sizes of the equipment required, and of course, insure unconditional fulfillment

of all process requirements. These models have been developed, and their use in application to different chemical complexes has proven to be highly effective.

Despite the fact that traditional solutions must be discarded practically completely, and a transition must be made to new, untested solutions, the total outlays of design time are decreasing due to minimization of all objects subject to development and the relationships between them. It is even more effective to use automated design methods employing computers and plotters.

Obviously optimization in the design stage also means a decrease in the material and energy outlays associated with erection of the complex. Also of no small importance is the decrease in the territory required. But the greatest impact is enjoyed, of course, in the operating stage.

#### Superoptimum Control

Quite recently only the work of large devices was automated, while today systems for controlling production operations of medium and low output and their individual devices have been created on the basis of minicomputers and microprocessors and are being widely introduced.

Cases are known in the practical work of chemical industry in which automation based on computers provided a return as early as in the course of start-up of a high-volume production operation. Introduction of automatic control systems is proceeding at an ever-increasing pace. It is believed that by the end of the century there will be no more unautomated chemical production operations. And if there had been serious debate in former times concerning the economic feasibility of automating small and medium-sized enterprises on the basis of computers, all stops were removed with the appearance of micro-computer technology. In other words automation is now advantageous practically everywhere.

We must not forget that it is usually much more difficult to create an automatic control system for a chemical production operation than similar systems in other sectors of industry. Despite the successes of mathematical modeling, the quantity of programs that can be used in relation to different production operations is relatively small for the moment. The reason for this lies in the complexity of the chemical process itself. For example the mathematical description of processes for refining mineral oils, which are not all that complex, contains 100-300 equations with 250-500 unknowns. But these are all temporary difficulties.

In comparison with manual labor, the productivity of "laboratory automatons" is 3 to 10 times higher. One computer can service any number of automatic analyzers installed both in the laboratory and on the apparatus of a chemical production operation. People are already talking about creating complex laboratory automatons that record all necessary parameters at any prescribed frequency. A thousand analyses per hour for example. Concurrently with growth in the speed of analysis, its accuracy increases. Before, the time of a chemical reaction was usually many times less than the analysis time.

Now we can say that the reverse relationship holds, which essentially opens up fantastic possibilities for recording all intermediate states of a substance and developing methods of "superoptimum" process control.

### Visible and Invisible Wastes

Intensification would be inconceivable without deeper processing of raw materials, and without an effort to achieve completely wasteless production. Without even going into the details of the savings to be enjoyed from selling an additional quantity of products, everyone can estimate the impact from reducing the outlays on doing away with production wastes. Recall those waste heaps--those mountains of "valueless" rock. But these are not just simply mountains. They are also labor, capital investments and equipment wear.

There are invisible wastes. They are colossal. These are wasted energy, chiefly thermal energy. Recycling of secondary energy resources in production has now become an important direction of intensification. Utilization of recycled heat in chemical industry tripled in the last decade. Many production processes based on the use of the energy of the excess pressure of products leaving the production operation, on the heat-producing capability of combustible gases and wastes, and on the heat of water, condensate, heated products and exothermic reactions, have been developed and introduced. Each of these forms of recycled energy resources are subdivided somewhat conditionally in relation to the levels of energy they contain. For example, the energy contained in the pressure of a product differs entirely if it leaves the production operation at 2 or at 20 megapascals. The apparatus used to trap this energy differs correspondingly as well.

It may be a surprise to many that about a third of all outlays go into drying various materials used in the world economy. One would think that drying is an insignificant process, far from being the most important. But practically all minerals are dried, and wood, most harvested agricultural crops and numerous chemical products are dried.

How are they dried? Over 70 percent of all products are dried with water vapor and hot water. This is why the steam supply system has become so significant in all major chemical production operations. The drying of about 20 percent of all products involves combustion of solid fuel--coal, peat, wood. About 85 percent of oil and gas is expended in one way or another on processes involving removal of excess liquid from a substance.

Chemical process engineers of the whole world are constantly working to improve filtration, evaporation and drying processes and to raise their effectiveness. The apparatus used for this purpose is undergoing continual improvement.

Apparatus in which drying proceeds in a fluidized or turbulent bed is enjoying increasingly greater applications. Equipment in which drying processes proceed simultaneously with the product's granulation is being created more and more frequently. One unit combines several different drying methods, including ones using all kinds of emissions--ultrasonic, acoustic, infrared. These are the main trends of today.

Because drying requires so much energy, high-volume enterprises will have to be moved in the future nearer to the sources of cheap thermal energy. This would signify solution of the problem of recycled energy resources on a global scale.

#### The Catalyst Menu

An enormous quantity of chemical products are synthesized just owing to the use of catalysts. Progress in chemistry would be impossible without continual renewal of the menu of catalysts and catalytic systems.

In the usual interpretation, intensification of processes presupposes enlargement or growth of some parameter--the pressure in the reactor, the temperature in the furnace, the rate of the reaction. But when the discussion turns to catalysts, everything can be turned around.

For example, new catalysts based on oxides of zinc, copper and aluminum used in methanol production permit a decrease in the working pressure from 30 to 10 MPa. Just a three-time decrease in pressure essentially means a revolution in production: The requirements on metal quality, the metal content of apparatus and pipelines and the requirements on welded seam control are reduced, less energy is expended, service is simplified, and much else. And all of this is owing to "unassuming" catalysts with higher activity and selectivity than before. In order that the reader might understand the full meaning behind this, let me recall that quite recently a pressure of up to 100 MPa (1,000 atmospheres) and a temperature of 300-400° were required for methanol acquisition.

Here is an even more amazing example. Cobalt catalyst has been used since ancient times to synthesize acetic acid. The process was carried out at a pressure of 50-60 MPa and a temperature of 300°C. With a new rhodium catalyst the required pressure is 20 times (!) lower, just 3 MPa, at a temperature of 100°. While developers designing installations employing the old procedure had to solve a mass of complex technical problems, the new production operation does not create any difficulties. The catalyst in a sense reduces the energy barrier that must be surmounted to begin the reaction. About 20 percent of all chemical products are now obtained catalytically.

But despite the occasionally astounding results, in comparison with similar processes occurring in nature, catalytic chemistry is still in its initial stage of development. Catalysts used by nature are hundreds and thousands of times better in relation to all indicators. This is precisely why chemical scientists unanimously assert that catalysis offers a great future for chemical industry. Its main findings and accomplishments still lie ahead.

Especially attractive from all points of view are processes occurring in unstable "perturbed" catalyst layers, for example in a fluidized bed. Inducement of "perturbations," chiefly by pulsations, is the latest and most promising method of intensifying many processes of big chemistry. Terms rarely encountered in scientific publications--"phenomenal events," "unprecedented results"--can be found in articles dealing with deliberately unstable and

unbalanced processes and with the associated oscillatory motions of particles, ions, radicals and molecules.

### And Without Catalysts?

Chemists are pinning major hopes today on radiation influences upon chemical processes and materials. Refinement of polyethylene by irradiation and "cross-linking" of its molecules have already become textbook examples, even though such processes have only been around for a little more than 20 years. In recent years radioactive emissions have been used successfully in 50 or so industrial production processes. It is interesting that the processes go on at all temperatures and pressures (including low ones), without catalysts, irrespective of the aggregate state of the irradiated substances. Radiation activates all molecules. As a result they enter into all kinds of reactions, sometimes unpredictable, to form side products. This is the main shortcoming of radiation chemistry. But the advantages are so large that the shortcomings are accepted.

For example, the method of radiation vulcanization of rubber, without sulfur, raises the thermal stability of articles to 300°C. Polymer-concrete obtained by irradiating ordinary concrete to which monomers had been added is frost-resistant, it is moisture-proof and, moreover, it has 4 times the strength. Radiation is being used successfully to obtain and sterilize drugs, and to produce dyes.

Over a hundred charged-particle accelerators in the world are being used for radiation chemistry.

Despite the relatively low hardness of articles made from plastics, resistance of production equipment to wear and corrosion has great significance. A recently developed method of ionic introduction of nitrogen into the surface layer of equipment is making it possible to reduce by several times the wear of molds and of pumps delivering raw material. The first ion introduction chambers had a volume of 60-100 cubic centimeters. Chambers with a diameter of up to 2.5 meters are being built today; this will make it possible to process articles with an area of several square meters.

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CSO: 1841/49

CONVEYER-BELT DRYER FOR TOXIC EXPLOSIVE MATERIALS

Moscow KHMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 9, Sep 85,  
p 8

OSINSKAYA, V. P., candidate of technical sciences, and ANDREYEVA, S. G.  
engineer

[Abstract] The Scientific Research Institute of Chemical Machines has designed a conveyer-belt dryer for toxic explosives. The dryer, now in mass production, is essentially a sealed tank assembly equipped with fire-quenching and explosion-preventing systems, with temperature control provided by recirculating air. Longitudinal and cross-section diagrams are provided of the 16.5 x 3.2 x 3.8 m assembly. The dryer has been tested with bentonite-kaolin mixtures, achieving a moisture reduction from 26 to less than 2% with an operating efficiency 450 kg/h of raw material, or 120 kg/k of extracted moisture. Figures 2.

[98-12172/12955]

UDC 541.124.7:541.128.13:542.943:547.211

METHANE OXIDATION IN TWO-PART REACTOR

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 11 Jun 84) pp 987-990

MINASYAN, V. T., GRIGORYAN, G. L. and NALBANDYAN, A. B., Institute of Chemical Physics, Armenian SSR Academy of Sciences, Yerevan

[Abstract] An analysis was conducted on the use of a two-part reactor for the oxidation of methane, with the reactor undergoing preliminary priming with HF, boric acid, and subsequent evacuation at 813°K for several days. The course of methane oxidation was monitored at 733°K under a pressure of 40 kPa in the quartz reactor. The experimental data showed that the form of the kinetic curves did not change with the use of the two-part reactor. However, the time required for achievement of maximum velocity was shortened. In addition, while the yield of methanol remained unaffected, production of hydrogen peroxide and formaldehyde diminished in the two-part reactor. These observations indicate that higher selectivity for methanol is possible though modification of reactor design. Figures 3; references 11: 8 Russian, 3 Western.  
[72-12172/12955]

## COAL GASIFICATION

### DEVELOPMENT OF COAL TRANSPORT URGED

Moscow PRAVDA in Russian 21 Oct 85 p 2

[Article by Gennadiy Yastrebtsov: "Transport Without Wheels"]

[Excerpts] In our country we are planning and building various transport systems, and creating specialized institutes, administrations, and other organizations. But the proportion of new types of transport in the total volume of transportation is still too small. Moreover, while the quantity of oil and gas pumped through pipes increases each year, you can't say the same about other large freights.

And coal? The Nagornaya Mine is in the Kuznetsk Coal Basin. It sends its output to the West Siberian Metallurgy Combine. So how is the "combustible rock" transported? It goes the 7 kilometers to the station in trucks, then it is reloaded into gondola railroad cars and travels the remaining 5 kilometers to the combine on the rails. It is long, expensive, and inconvenient.

Meanwhile, there is a fundamentally different system operating in the very same Kuznetsk Coal Basin. Yubileynaya and Inskaya mines have laid down coal lines to Zapsib and Belovskiy State Rayon Electrical Station, respectively. Millions of tons of fuel are transferred to their destination much more rapidly and inexpensively. Such pipelines have been known of for a long time. But they have substantial shortcomings: they consume a great deal of energy and the tubes wear out fast. Other technical solutions are needed to move the raw materials for significant distances: for example, the tube passes a specially prepared fine-dispersion pasty pulp. The rate of movement is not high, so this method is more economical and the wear and tear on the equipment is less....

### Running in Place

In 1978 an expanded session of the board of the USSR Gosplan discussed the question of the future of laying down the Belovo-Novosibirsk Main Coal Pipeline. The direction was not chosen by accident. While the total volume of railroad transportation increased by 9 percent in the 12th Five-Year Plan, the flow of loads from the Kansk-Achinsk and Kuznetsk coal basins increased by 12 percent. How to get the fuel out rapidly and without losses? That is where the Belovo-Novosibirsk hydrotransport system would help. It would extend for 250 kilometers, and its projected productivity is 3 million tons per year.

But the effort is moving too slowly. In 1983-1984 organizations of the USSR Ministry of Coal Industry and Ministry of Construction of Petroleum and Gas Industry Enterprises fulfilled only 1.8 million rubles' worth of construction-assembly projects with a plan of 16.6 million. Practically no coal or energy workers have come to work on construction projects of the pipeline, although the USSR Gosplan fully provides this important project with capital outlays. Moreover, the line has been permitted to be laid down according to individual sketches and estimates, not waiting for confirmation of the entire project.

Now, in order to move the construction out of a standstill, the Ministry of Construction of Petroleum and Gas Industry Enterprises has taken the designing on itself, since the Ministry of Coal Industry did not fulfill its functions either as a client or as a general designer.

Certain ministries and departments, it appears, underestimate the technical and economic usefulness of continuous types of transport. Otherwise how do you explain the fact that a number of planned facilities have not been constructed in the scheduled periods, and those which were put into operation could not make the projected capacity for long?

Take the Ministry of Construction of Petroleum and Gas Industry Enterprises. In this sector they spend quite a bit of time studying new forms of continuous transport. They have created a hydrotransport administration and the All-Union Scientific-Research and Design Institute of Hydropipelines in Moscow with branches in Tbilisi, Donetsk, and Novokuznetsk. They created the Soyuztransprogress All-Union Industrial Association, one of whose elements is the All-Union Scientific-Research and Design Transprogress Institute with an experimental base and testing field in the Moscow suburb Ramenskoye.

The prospects for "transport without wheels" are great. Experts of the USSR Gosplan are now studying the problem of creating a major pipeline from the Kuznetsk Basin to the Urals. It will be more than 2,000 kilometers long, capable of transporting 33 million tons of coal per year. Bypassing the railroads, the coal energy will go through pipes to thermal electric power stations and metallurgy enterprises of one of the largest industrial regions of the country.

The board of the USSR Gosplan entrusted the Institute of Integrated Transport Problems and Institute of Integrated Fuel-Energy Problems with drafting a joint technical-economic paper on choosing the form of transport for moving coal from the Kuznetsk Basin to the European part of the country. And what became of it? Instead of the paper agreed upon, the scientists came up with very contradictory, "disjointed" proposals to be sent to a panel of experts. That is the kind of integrated approach here....

12255  
CSO: 1841/67

COMBUSTION

UDC 541.127:542.921.7:546.281.027

ISOTOPE EXCHANGE IN THERMAL DECOMPOSITION OF  $\text{SiH}_4$ + $\text{SiD}_4$  MIXTURE

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 20 Jul 84) pp 790-798

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[Abstract] Studies were conducted on isotope exchange in thermal decomposition of  $\text{SiH}_4$ + $\text{SiD}_4$  mixtures in order to differentiate between molecular and radical chain reactions as the mechanism responsible for this process. Studies with the 4% mixtures were conducted in argon under a pressure of 300-1000 Pa and a temperature range of 400-500°C. Mass spectrometry demonstrated that the isotope effect in thermal decomposition of this compound was minimal, indicating that for all practical purposes  $[\text{SiH}_4] = [\text{SiD}_4]$  not only for the original mixture, but at any time during thermal decomposition. The fact that appearance of  $\text{SiH}_3\text{D}$  and  $\text{SiHD}_3$  preceded the appearance of  $\text{SiH}_2\text{D}_2$  led to the following formulation for the sequence of appearance of mixed deuteriosilanes:  $\text{SiH}_4 \rightarrow \text{SiH}_3\text{D} \rightarrow \text{SiH}_2\text{D}_2 \leftarrow \text{SiHD}_3 \leftarrow \text{SiD}_4$ . The kinetic and spectrometric data were compatible with a predominantly molecular mechanism involving the transfer of one hydrogen (or deuterium) atom. Figures 5; references 15: 2 Russian, 13 Western.  
[75-12172/12955]

UDC 541.127:546.11-123:547.234:543.42.27

REACTION KINETICS OF ATOMIC HYDROGEN-HYDRAZINE INTERACTION

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 26 Jun 84) pp 990-991

CHOBANYAN, S. A., MKRYAN, T. G. and SARKISYAN, E. N., Institute of Chemical Physics, Armenian SSR Academy of Sciences, Yerevan

[Abstract] ESR studies were conducted on the reaction kinetics of atomic hydrogen with hydrazine at 304-505°K, within a pressure range of 0.23 to 0.33

kPa. Analysis of the reaction products indicated that the predominant reaction involved disruption of the N-H bond,  $H + N_2H_3 \rightarrow N_2H_2 + H_2$ , and was accompanied by the secondary reaction  $N_2H_2 \rightarrow N_2 + H_2$ . On the basis of the rate constants at different temperatures, which ranged from  $1.08 \times 10^{-11} \text{ cm}^3/\text{mole}\cdot\text{sec}$  at  $304^\circ\text{K}$  to  $4.32 \times 10^{-11} \text{ cm}^3/\text{mole}\cdot\text{sec}$  at  $504^\circ\text{K}$ , the following linear equation for the rate constant was derived:  $k = (4.1 \pm 0.6) \times 10^{12} \exp[(-9.2 \pm 0.9)/RT] \text{ cm}^3/\text{mole}\cdot\text{sec}$ . Figures 1; references 9: 3 Russian, 6 Western.

[75-12172/12955]

ELECTROCHEMISTRY

UDC 541.138.2

EFFECTS OF SELECTIVE ADDITIVES ON ANODAL OXIDATION OF SINGLE CRYSTAL SILICON  
IN NITRATE MELTS

Moscow ELEKTROKHIMIYA in Russian Vol 21, No 8, Aug 85  
(manuscript received 17 Oct 83) pp 1022-1027

SHIRSHOV, Yu. M., STEPANOVA, I. A., VASILEVSKAYA, T. B. and CHERNUKHIN, S. I.,  
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[Abstract] A study was conducted on the effects of various additives on the anodal oxidation of silicon crystals serving as semiconductors in  $\text{KNO}_3\text{-NaNO}_3$  1:1 melts at 230-250°C, and on the physicoelectrical properties of the  $\text{SiO}_2$  films. Formation of the  $\text{SiO}_2$  film as a result of anodal oxidation of single silicon crystals proceeded with an energy of activation of 4 kJ/mole. The film was homogenous and had a refraction index of 1.46. Graph data are presented on the effects of addition of  $\text{Na}_2\text{MoO}_4$  in concentrations of 0.02 to 0.1 wt% on the potential-dependent characteristics of film formation. Addition of  $\text{Na}_2\text{MoO}_4$  led to a decrease in the thickness of  $\text{SiO}_2$  film in relation to applied anodal current due to changes in the mechanism of oxidation, and alterations in the hysteresis indicated by C vs. E plots. The findings indicated that the process of dielectric polarizaiton becomes the predominant factor on addition of  $\text{Na}_2\text{MoO}_4$ . Electrophysical determinations of the injected charge density and surface electronic states of the Si- $\text{SiO}_2$  system by means of a mercury probe demonstrated the beneficial effects of  $\text{Na}_2\text{MoO}_4$  addition. Figures 6; references 14: 5 Russian, 9 Western.

[046-12172/12955]

ELECTRIC SURFACE PROPERTIES OF ACTIVATED CHARCOALS USED IN HEMOSORPTION

Moscow ELEKTROKHIMIYA in Russian Vol 21, No 8, Aug 85  
(manuscript received 5 Sep 83) pp 1038-1043

SIGAL, V. L., NIKOLAYEV, V. G. and OSADCHIY, P. V., Institute of Oncological Problems imeni R. Ye. Kavetskiy, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] The electrical surface properties of activated charcoals used in hemosorption were analyzed by means of microscopic electrophoresis. Analysis of the mobility data and the calculated zeta potentials for KAU-K-0.7, SKN-68-M, SKN-70-80, SKN-2-M, SUGS-119, STN-90 and SKT-6A demonstrated that satisfactory results were not obtained either with Henry's equation or the conventional Smoluchowski approach. The electrokinetic characteristics of the activated charcoals under study were best described by the Simonov-Shilov equation [Simonov, I. N., et al., Dokl. AN Ukr. SSR, No 6-B:556, 1974]. The data confirmed the impression that regardless of the method of preparation, activated charcoal intended for clinical use bears a net negative charge, largely due to selective adsorption of  $\text{Cl}^-$  and dissociation of functional acid groups on the absorbent. As a result, such adsorbents are particularly effective in the uptake and removal of various cationic entities (e.g., positively charged proteins,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ , etc.). The electrophoretic mobility of the charcoals in question did not differ by more than 25% under the experimental conditions employed, indicating relative similarity in adsorbent effectiveness. References 20: 16 Russian, 4 Western.

[046-12172/12955]

UNIVERSAL GAS ABSORBER FOR AIRTIGHT ALKALINE BATTERIES

Moscow ELEKTROKHIMIYA in Russian Vol 21, No 8, Aug 85  
(manuscript received 2 Jan 84) pp 1085-1088

TSEENTER, B. I. and LAVRENOV, V. M., Leningrad

[Abstract] Schematic and mathematical description is provided of a universal gas absorber for use in alkaline batteries with an airtight seal. The basic scheme consists of serially arranged nickel-gas matrix elements, that are electrolytically isolated from one another and yet share a common gaseous space. The gas electrode of the nickel-gas element, the nickel oxide component of which is a metalloceramic entity, functions both in the ionization of oxygen and in the ionization of hydrogen, eliminating the need for venting. In the case of the silver-zinc battery the ratio between the nickel-gas and silver-zinc elements, connected in parallel, falls in the range between 1.6 and 2.0 for optimal function. Figures 3; references 2: 1 Russian, 1 Western.

[046-12172/12955]

UDC 541.13

DUAL EFFECTS OF ADSORBED POLYMERIC HYDROXIDE FILMS ON RATES OF ELECTRODE PROCESSES

Moscow ELEKTROKHIMIYA in Russian Vol 21, No 8, Aug 85  
(manuscript received 6 Jul 84) pp 1123-1126

ZAKHARKINA, P. S. and KORSHUNOV, V. N., Moscow State University imeni M. V. Lomonosov

[Abstract] An analysis was conducted on the effects of oxidehydroxide polymeric films formed on electrodes during hydrolysis of  $\text{Er}^{3+}$  cations on  $\text{Na}(\text{Hg})$  and rotating Zn disc electrodes. The  $i$  vs.  $t$  plots in 1 M  $\text{LiCl}$  and 1 M  $\text{NaCl}$  with and without addition of  $10^{-3}$  M  $\text{ErCl}_3$  in the case of Hg electrodes, and in 0.1 M  $\text{Li}_2\text{SO}_4$  with and without  $\text{Er}_2(\text{SO}_4)_3$  or  $\text{ZnSO}_4 + \text{Er}_2(\text{SO}_4)_3$  in the case of the Zn electrode, demonstrated that such films exert a dual effect on the rates of the various reactions on the electrodes. If the depolarizing agent is a proton donor the films function as catalytic matrices and promote hydrogen gas release. However, in the case of discharge ionization of metals such films act as inhibitors, with the degree of inhibition proportional to the degree of hydration of the metal ion. Figures 2; references 16: 1 Polish, 9 Russian, 6 Western.

[046-12172/12955]

UDC 541.138.3

ELECTROCHEMICAL REDUCTION OF CHLOROPHYL IN COLLOID SOLUTIONS

Moscow ELEKTROKHIMIYA in Russian Vol 21, No 8, Aug 85  
(manuscript received 6 Jul 84) pp 1143-1146

SUPONEVA, Ye. P., KAZAKOVA, A. A., KADOSHNIKOVA, I. G. and KISELEV, B. A., Institute of Pedology and Photosynthesis, USSR Academy of Sciences, Pushchino

[Abstract] Polarographic and fluorescence studies were conducted on the electrochemical reduction of chlorophyl in the colloid state in a system designed to simulate molecular organization of the pigment molecules in a photosynthetic apparatus. Employing phosphate buffers with 0.05-0.1% Triton X or 0.05-1% acetone led to results indicating that chlorophyl is capable of self-aggregation into molecular complexes. In such associations or complexes, the parameters of quasireversible electrochemical reduction indicated that the anion-radicals of the pigment ( $\text{Chl}^{\cdot-}$ ) have a fairly long half-life. The increase in the stability of  $\text{Chl}^{\cdot-}$  has been ascribed to delocalization of the negative charge in the aggregates in comparison with the monomeric state of chlorophyll, as well as to extrusion of water and reduction of the dielectric constant within the aggregate (colloid) milieu. Both factors diminish the rate of  $\text{Chl}^{\cdot-}$  protonation, resulting in an increase in its lifetime. Figures 3; references 15: 11 Russian, 4 Western.

[046-12172/12955]

USE OF CHARCOAL FOR ENZYME ELECTRODES

Moscow ELEKTROKHIMIYA in Russian Vol 21, No 8, Aug 85  
(manuscript received 19 Jul 84) pp 1147-1149

BOGDANOVSKAYA, V. A., GAVRILOVA, Ye. F., SHIMSHLEVICH, Ya. B., YAROPOLOV, A. I. and GINDILIS, A. L., Institutes of Electrochemistry imeni A. N. Frumkin and of Biochemistry imeni A. N. Bakh, USSR Academy of Sciences, Moscow

[Abstract] Various charcoals were tested for their efficiency and suitability for providing a solid support for immobilized enzyme electrodes promoting oxygen electroreduction. Studies with laccase derived from *Polyporus versicolor* showed that optimum retention of enzyme activity and highest specific activity was obtained with activated charcoal BM-4. BM-4 is characterized by high mesopore volume ( $0.73 \text{ cm}^3/\text{g}$ ) and protein binding capacity (31 mg/g). Polarization curves for electroreduction of oxygen demonstrated that with anodal current BM-4 corrosion was extensive at positive potentials as low as 0.9 V, while a potential of 1.3 V leads to irreversible inactivation of the enzyme electrode. In cathodal reduction of oxygen, increase of the cathodal current at low degrees of polarization has virtually no effect on the electrode potential in citrate buffer, pH 5.0. Figures 4; references 6: 4 Russian, 2 Western.

[046-12172/12955]

ELECTROLYTIC REDUCTION OF SILICON COMPOUNDS IN MOLTEN  $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-SiO}_2$

Kiev UKRAINSKIY KHMICHESKIY ZHURNAL in Russian Vol 51, No 8, 1985  
(manuscript received 20 Oct 83) pp 826-830

PRUTSKOV, D. V., ANDRIYKO, A. A., DELIMARSKIY, Yu. K. and CHERNOV, R. V., Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Chromopotentiometric and other methods were used to assess electrolytic reduction of silicon compounds in  $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-SiO}_2$  melts at 900°C, with the concentration of  $\text{SiO}_2$  ranging from 0.1 to 1.5 wt%. With concentrations of 0.5 wt% or less three diffusion waves were obtained (-0.32, -0.47, and -0.65 V) indicating that the most stable intermediates were Si(II) and Si(I) compounds. The equilibrium constant for the reaction  $\text{Si(IV)} + \text{Si(II)} \rightleftharpoons 2 \text{Si(III)}$  was less than  $10^{-2}$ , suggesting that the concentration of Si(III) compounds in the melt was insignificant. The phase composition of the deposits at the potentials of the first (-0.32 V) and the second (-0.47 V) waves was essentially identical to the composition of the passivating layer on liquid aluminum in cryolite melts, with the dispersed particles of pure Si in the deposits ranging from 5 to 20  $\mu\text{m}$ . The cathodal deposit at the

potential of the third wave (-0.65 V) contained, in addition, large, needle-shaped Si crystals 50 to 200  $\mu\text{m}$  in size, which represent the primary products of electrolytic reduction. The overall reaction can be described as  $[\text{SiO}_2]_n \xrightarrow{2e^-} \text{Si(IV)} \xrightarrow{e^-} \text{Si(II)}_s$ , with  $\text{Si(II)} \xrightarrow{e^-} \text{Si(I)} \xrightarrow{e^-} \text{Si(0)}$  and  $\text{Si(II)} \xrightarrow{e^-} \text{Si(II)}_s$ . Figures 3; references 17: 1 Czech (in English), 13 Russian, 3 Western.  
[045-12172/12955]

UDC 53.987.92:612.122.1:621.352.6

DETERMINATION OF GLUCOSE CONCENTRATIONS IN BIOLOGICAL SAMPLES BY ELECTRO-CHEMICAL OXIDATION

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 8, 1985  
(manuscript received 11 Mar 84) pp 845-848

VOLOSHIN, A. G., TETERIN, G. A., KOLESNIKOVA, I. P., METELICHENKO, B. L., KAPENASYUK, N. S., KALYUZHNAIA, Ye. A., MUNTYAN, G. I., SEID-GUSEYNOV, A. A. and KALIKHMAN, V. L., Odessa State University

[Abstract] Cursory description is provided of a biofuel cell for the electrochemical assay of glucose concentration in biological samples. The method relies on the correlation between the current generated by glucose oxidation on the anode and the concentration of glucose in the sample, concomitant with the reduction of atmospheric oxygen on the cathode. Trials with serum samples, blood, and Krebs-Ringer solutions demonstrated this to constitute a reliable approach to glucose analysis that offered a number of advantages over the more complex and labile immobilized enzyme electrodes. At ca. 20°C the system functioned reliably for 120-150 hrs with blood samples and for over 400 days with Krebs-Ringer solutions, with a response time on the order of 2-3 min. Figures 5; references 11: 3 Russian, 7 Western.  
[045-12172/12955]

UDC 661.416.1.001.57

APPLICATION OF MATHEMATICAL MODELLING IN ANALYSIS OF TECHNOLOGICAL SYSTEMS, CONSTRUCTION AND INTENSIFICATION OF CHLORINE DIAPHRAGM ELECTROLYZERS

Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 8, 1985 pp 459-466

KHEYFETS, L. I. and GOLDBERG, A. B.

[Abstract] Practical results of the use of mathematical modelling are reported as applied to the analysis of diaphragm chlorine electrolyzers with vertical electrodes. In general, development of a mathematical model system includes the following aspects: systematization of physical-chemical data, analysis of the characteristics of the range and duration of the process,

analysis of individual stages in each process, synthesis of an overall algorithm for calculation of mass and heat flow, programming aspects, data input and analysis of the results. The following topics were discussed: current problems; general method of the calculation of cell voltage drop and distribution of current density on the surface of an electrode; hydrodynamic model of gas filling in circulating stream of an electrolyte; similarity criteria of the electric fields in electrolyzers; intensity of secondary processes and selection of quantitative values for modelling; justification for accurate assembly of electrode complex; effect of electrode height on the current yield and voltage drop; maximal decrease of the energy use by selection of the thickness of a diaphragm; application limits for the use of modified diaphragms; calculation of the acidification regimen and the effect of brine concentration on current yields. Figures 9; references 51: 22 Russian, 29 Western.

[61-7813/12955]

## EXPLOSIVES AND EXPLOSIONS

UDC 678.544.2.049.13:539.3

### EFFECT OF RATIO OF COMPONENTS ON TRANSITION TEMPERATURES AND PHYSICAL AND MECHANICAL PROPERTIES OF NITROCELLULOSE-BASED COMPOSITE MATERIALS

Kiev KHMICHESKAYA TEKHOLOGIYA in Russian No 4, Jul-Aug 85 (manuscript submitted 20 Oct 83), pp 29-31

[Article by S. S. Pelishenko, P. I. Demchenko, L. G. Bogodist, V. S. Sanatulin, P. I. Aleksanov, I. A. Uskov: "The Effect of the Ratio of Components on Transition Temperatures and the Physical and Mechanical Properties of Nitrocellulose-based Composite Materials"]

[Text] The swelling of composite materials based on nitrocellulose (NC), used for making nitrolinoleum, has been previously studied [1]. Hypotheses have been expressed about the compatibility of the components in the systems studied. The basic requirements imposed on linoleum materials are stability of operating characteristics over time, low shrinkage, sufficient resistance to cold, and high strength while maintaining a capacity for deformation.

In this work, the thermomechanical properties and strength of NC-based composites were examined and optical microscopic studies of the structure of the composites were conducted. Three-component systems were chosen as research objects, with a mass content of 40 to 70% NC, 5 to 30% SKN-26 or SKN-40 butadiene-nitrile rubber, and 30% low-molecular dibutyl phthalate (DBF) plasticizer. The DBF content in the composites remained constant, which was due to the production method for obtaining the test pieces -- rolling. Rolling was done in laboratory rollers--with the rollers heated to  $80 \pm 5$  C--for 25 to 30 minutes. The test pieces for the thermomechanical studies were made by cold pressing in the shape of pellets 2 mm thick and 10 mm in diameter. Test pieces of a uniform size for the physicomechanical studies were stamped from the rolled sheet. Test pieces for the optical microscopic studies were slices 50  $\mu$  thick, obtained from the rolled sheets using a special device.

The thermomechanical (TM) curves were plotted by the method described in reference 2. Preliminary studies showed that the thermomechanical curve has the most distinct shape if measurements are taken at a constant loading of  $7.65 \text{ kg/cm}^2$ . The thermomechanical curves, from which the glass-transition temperature ( $T_g$ ), softening temperature ( $T_s$ ), amount of deformation in the glassy-state region ( $E_{gl}$ ), and maximum deformation ( $E_{max}$ ) were plotted at this constant loading value. The amount of deformation was taken every 2 degrees, and every degree in the transition region. In every case, not less

than three TM curves were plotted, and deviations between transition temperatures were not more than 1 degree. Bursting strength ( $\sigma_b$ ) and elongation when stretched ( $\epsilon$ ) were determined according to the standard method in OST [All-Union Standard] 84-306-70, with a stretch rate of 30 mm/min.

The optical microscopic studies were conducted in transmitted and reflected light using a standard polarizing microscope. The structure was studied at 63 to 250 magnifications. Photomicrography was obtained using a photomicrographic attachment and a camera, at 125 magnifications.

Figure 1 shows TM curves of compositions containing different amounts of SKN-40 rubber. As is evident from the illustration, when the rubber content increases  $T_g$  and  $T_s$  shift to the lower temperature region, and deformation sharply increases. Similar results were obtained for compositions with SKN-26 rubber added. Analysis of the data shown in the table makes it possible to draw the conclusion that with all of the ratios of components studied, NC-based compositions are characterized by one glass-transition temperature. This indicates compatibility of components. In the TM curves for compositions containing a comparatively small amount (5%) of added rubber, a significant point spread is observed, which may be explained by the uneven distribution of the components at this rubber content when the test samples are obtained by rolling.

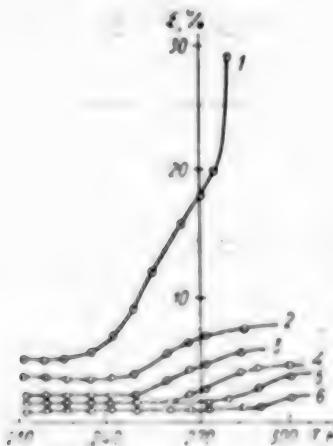


Figure 1. Thermomechanical Curves for NC-BDF-SKN Compositions Containing 100 (1), 30 (2), 25 (3), 20 (4), 15 (5) and 5% (6) SKN-40

Nitrocellulose, as a rigid-chain polymer, is characterized by low deformation capacity (see table). The introduction of the low-molecular plasticizer DBF increases NC deformation in the glassy state insignificantly (from 0.5 to 1.5%); the material remains brittle, incapable of significant deformation, and is shattered at low loadings. The addition of rubber to plasticized NC (beginning with a composition containing 15% SKN) leads to a sharp increase in maximum deformation in the glassy-state region. From this point on,  $E_{max}$  and  $E_{gl}$ , in the range of concentrations of added rubber studied, depends

little on the content of added rubber in the composition. A substantial difference was not observed in the deformation capacity of compositions containing rubber additives with a varying content of bonded acrylonitrile.

Table. Results of Thermomechanical Studies

Content of Components in Composition, %			T <sub>g</sub> , K	T <sub>g</sub> , K	E <sub>max</sub> , %	E <sub>gl</sub> , %
NC	DBF	SKN	SKN-40 SKN-26	SKN-40 SKN-26	SKN-40 SKN-26	SKN-40 SKN-26
100	---	---	353	---	---	0.5
65	30	5	288/325	336/363	11/9	1.5/1
60	30	10	288/313	327/353	52/18	1.5/1.5
55	30	15	272/286	322/341	75/42	2/1.5
50	30	20	267/272	321/335	200/270	3/2
45	30	25	261/255	320/331	360/340	4/8
40	30	30	254/251	318/320	415/430	5/12
---	---	100	247/230	287/278	760/730	18/14.5
70	30	---	268	---	---	1.5

It is interesting to examine the mechanism of effect of modified additives on NC. It is known [3] that DBF is a good NC plasticizer. However, despite the fact that T<sub>g</sub> declines in a straight line when the DBF content is increased to 30%, the material retains significant rigidity, as was shown above. This, apparently, can be explained by the different capacity of the nitrogens, located on the surface of the spiral conformation of the macromolecule and within it, to interact with DBF molecules and, consequently, by the different capability of the latter to weaken the molecular interaction in the NC. On the other hand, the systems studied contained rubber, which also can be plasticized by DBF. Here, it is true that the plasticizer has a greater effect on SKN-40 than on SKN-26, since the former has a higher content of bonded acrylonitrile. In addition, as evidenced by thermomechanical analysis of the three systems, rubbers have a plasticizing action with regard to NC, since the T<sub>g</sub> of the composition shifts to the low temperature region when the rubber content is increased.

Figure 2 shows T<sub>g</sub> as a function of the ratio of components (NC : SKN) with a constant mass content of DBF at 30%. The points are well placed in a straight line both in the case of the composition containing SKN-26, as well as the composition with addition of SKN-40. Extrapolation of the linear functions obtained at the zero content of NC should yield the T<sub>g</sub> of the initial rubber. The experimentally determined glass-transition temperatures are 230 K for SKN-26 and 247 K for SKN-40, which agrees with reference data.

The greater the effectiveness of the plasticizing additive, the greater the degree of lowering of T<sub>g</sub> of the composition. Thus, in the systems studied, SKN-40 was more effective at low concentrations of rubber in comparison with SKN-26. This is associated with the fact that DBF has a more effective action on the more polar, i.e., containing the greatest amount of bonded

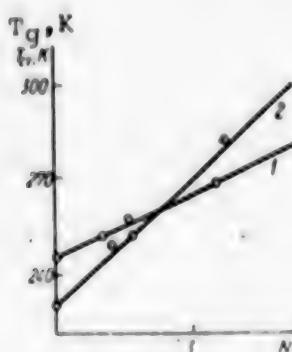


Figure 2. Glass-Transition Temperatures as a Function of the NC : SKN Ratio for Compositions Containing SKN-40 (1) and SKN-26 (2)

acrylonitrile rubber and, in the triple system, the total plasticizing effect is higher. SKN-26, containing a lower amount of polar groups, is plasticized by DBF to a lesser degree, although it mixes with NC well. NC polar groups are blocked by SKN-40 polar groups to a greater degree than SKN-26 polar groups and, although their compatibility is about the same, SKN-40 more effectively affects NC. When the content of rubbers in the system is increased, a greater influence of SKN-26 on NC is observed, in comparison with SKN-40. This, apparently, is associated with the fact that the compatibility of SKN-40 with NC at high concentrations is less than the compatibility of SKN-26 with NC.

Direct information on the structure of NC compositions can be obtained using the optical microscopic method. Figure 3 shows photomicrography of the samples studied. Structural heterogeneity was found in a composition of NC and 30% DBF (Figure 3, a), which, in our opinion, is explained not by the presence of DBF, which forms a single-phase system with the NC [3], but by the structural heterogeneity of the polymer itself. A study of this composition in polarized light shows the double refraction, which indicates the presence of some amount of crystalline formations. As is evident from the illustration, the structure of the NC-DBF composition is of small-sized aggregates of from 15 to 20  $\mu\text{m}$ .

Introduction of small amounts of SKN-26 (5%) into the composition only slightly affects the character of the NC structural organization (Figure 3, b). With an increase in the rubber content, the structural heterogeneities become significantly less expressed. However, when the content of SKN-26 in the composition is greater than 15%, there is a sharp change in the structure of the material (Figure 3, c): heterogeneity is maintained, but the aggregates become significantly larger in size (from 40 to 50  $\mu\text{m}$ ). When the SKN-26 content is increased from 20 to 30% (Figure 3, d), the boundaries of the aggregates become more blurred and there is interpenetration of structural elements belonging to the different components. The nature of the effects of rubbers containing different amounts of bonded acrylonitrile on the structure of NC-based compositions are practically identical. However, structural heterogeneity of the composition is found at a lower content of

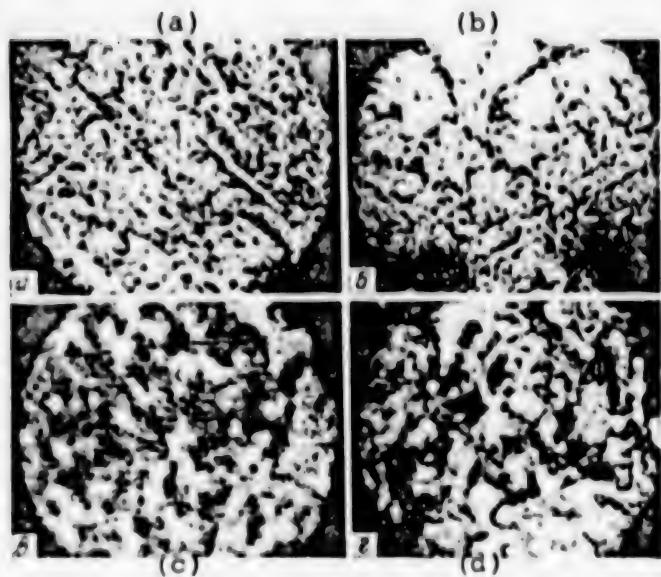


Figure 3. Structure of Cross-sections of NC-DBF-SKN-26 Compositions Containing 0 (a), 5 (b), 20 (c), and 30% (d) SKN-26

SKN-40 rubber, as compared with compositions containing added SKN-26, which is proof of the better compatibility of the latter with NC. This agrees with results of research into the compatibility of the components of NC compositions obtained by the swelling method [1].

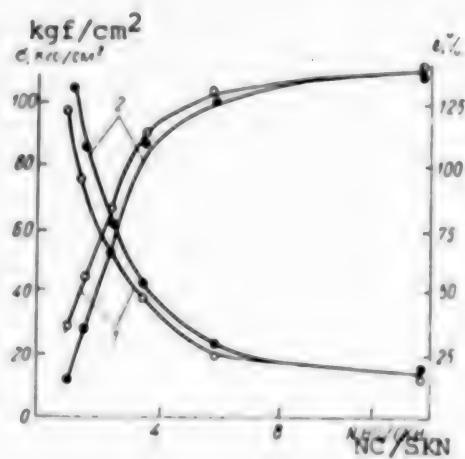


Figure 4. Strength During Stretching ( $\sigma_b$ ) and Elongation ( $\epsilon$ ) of NC-DBF-SKN Compositions Containing SKN-40 (1) and SKN-26 (2) as a Function of the NC : SKN Ratio

Along with the determination of  $T_g$ , a study was done of the strength and elasticity of a nitrocellulose composition when SKN-26 and SKN-40 were added. Analysis of these data shows (Figure 4) that the indices of strength and elasticity of the composition with a rubber content of up to 15% were practically independent of the bonded acrylonitrile content. Here, the strength of the composition was reduced by about 20%, and elasticity did not increase more than three-fold. When the rubber content is increased above 15%, elasticity of the composition with SKN-26 is somewhat higher, and strength lower, than for that containing SKN-40.

Thus, based on experimentally obtained data, the optimum formulations of NC-based compositions containing both low-molecular and high-molecular additives were determined and the nature of their effect on the structure and properties of such compositions were shown.

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Kiev University

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12304  
CSO: 1841/4

FERTILIZERS

BRIEFS

MINERAL FERTILIZER PLAN OVERFULFILLED--Kokand--The collective of Kokand Super-phosphate Plant has begun shipping mineral fertilizers produced above the five-year targets. The chemists' timely fulfillment of this important point of socialist obligations helped in the technical reoutfitting of production. New highly productive equipment made it possible not only to sharply increase the output of mineral fertilizers, but also to raise the quality of the goods supplied to republics of the country. [By R. Tell] [Text] [Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 3 Oct 85 p 2] 12255

CSO: 1841/67

SELECTIVITY OF ADSORPTION OF HUMIC ACIDS OF PEAT ON MONTMORILLONITE

Minsk VESTNIK AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHMICHESKIKH NAUK  
in Russian No 4, 1985 (manuscript received 14 Aug 84) pp 15-20

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[Abstract] A study is reported on the selectivity of adsorption of fractions of humic acids, enriched in aromatic and aliphatic fragments, on clay minerals. Montmorillonite was chosen as a representative mineral finely dispersed in typical soils and sedimentary rocks. The humic acids were divided into fractions using a 60:40 acetone-water mixture, which dissolved most of the aromatic fragments, as verified by infrared spectrometry. Under static conditions, a 0.1% water solution of the humic acid fraction was held for two weeks in contact with a measured amount of montmorillonite. The fraction soluble in the acetone-water mixture showed the lowest adsorption for sedge peat. Adsorption under dynamic conditions was carried out by passing the humic acid solution through a layer of the mineral until the optical densities of the incoming and exiting streams were equal. This resulted in somewhat higher adsorption, probably due to the constant concentration of the incoming solution. Electron paramagnetic resonance spectra showed narrower lines for the soluble fraction, apparently because of a higher content of condensed aromatic structures. Infrared spectra showed little difference in the basic structural elements present in the humic acids of sedge and reed peats. The insoluble fractions were enriched in hydrocarbon and amide groups, while the soluble fractions showed significantly more carboxyl groups. Although humic acid samples passed through the montmorillonite were contaminated with the mineral, analysis did indicate that the adsorption is primarily aliphatic molecules with polar structures which are able to partially penetrate into the inter-layer spaces of the montmorillonite or are adsorbed on the surface. Figures 2; references 4 (Russian).

[29-12672/12955]

BOOK: PHYSICAL CHEMICAL ASPECTS OF PRODUCING NEW FORMS OF FOOD

Moscow KHIMIYA: ROL KHIMII V RAZRABOTKE PERSPEKTIVNYKH METODOV POLUCHENIYA PISHCHEVYKH PRODUKTOV in Russian No 8, 1985 (signed to press 23 Jul 85) pp 30-34

[Article is Item 5, from Source by Vladimir Borisovich Tolstoguzov, professor, doctor of chemical sciences, head of laboratories of Order of Lenin Institute of Elementoorganic Compounds imeni A.N. Nesmeyanova, USSR Academy of Sciences, Moscow, Znaniye, 1985]

[Text] This section contains information about scientific approaches which are most applicable to the development of the new sector of food production.

The technology of production of new forms of food includes two stages. The first stage includes separation of protein and other food substances from various traditional and new forms of food raw material. The second stage involves conversion of proteins and a mixture of other food substances into new food products. Food proteins obtained at the first stage, just as lipids, polysaccharides and other ingredients, are not food in and of themselves but are merely food components. Therefore, in order to make proteins and other food substances suitable for use in the public diet, they must be reprocessed, in the second stage, into attractive and palatable foodstuffs for the consumer. Scientific aspects of both of these stages are closely interrelated. The first stage involves fractionation of the food raw material, i.e., production of protein and other foodstuffs from a multi-component and heterogeneous protein-containing system while the second stage involves production of a food product, i.e., a multi-component system which now has desirable composition, structure and physico-chemical properties. In view of this, two circumstances must be considered.

First, the process of producing a new food product usually includes two stages because the overwhelming majority of food products are solids, containing 50-90 percent water. Gels possess such a combination of composition and properties. In other words, from the point of view of physical chemistry, most food products are gels with specific composition, structure and complex of physico-chemical properties. The two-stage nature of their production follows from this. At the first stage, a multi-component liquid food system is produced and, at the second stage, this system is formed and converted from a liquid into a solid gel-like state, thus fixing the form and the macrostructure and ensuring the presence of the required properties in the finished food product. We may cite, as examples of this, the formation and gelation of granules for production of analogs of fresh caviar, groats and berries and formation and gelation of combined meat stuffings for production of articles from processed meat etc.. Another

important part of the new food products is liquid dispersed systems (food emulsions which are analogs of milk and dairy products, for example), the processes of production of which are, basically, one-stage processes. However, the gel-like state of food products may also play an important role in stabilization of these dispersed systems by forming solid layers at the interface of phases and thus producing a structural-mechanical barrier which prevents coalescence of the dispersed particles.

Second, it is important to realize that both food raw material and food products, being multi-component systems, contain, in most cases, two basic types of macromolecular substances: proteins and polysaccharides. Both of these components perform important structural functions as well as nutritional functions in food systems. Therefore, the behavior of proteins and polysaccharides has a predominant influence on the structure, physico-chemical properties, possibilities of composition variation and properties of processed food systems and food articles prepared from them. For these very reasons, problems of complex formation, thermodynamic compatibility and gelation of proteins and polysaccharides in aqueous media and also their capacity to stabilize foams, emulsions and other complex dispersed systems and to form isotropic and anisotropic gels with the properties, macrostructure and properties required are of utmost importance in attempts to develop scientific bases for production of new forms of food. Actually, we are talking about the regulation of functional properties of proteins and polysaccharides and mixtures of them in order to ensure reprocessing of protein for inclusion in diverse food systems and, possibly, to expand the assortment of available food products. Under conditions of limited thermodynamic compatibility of proteins with other proteins or of proteins with polysaccharides, these macromolecular components are concentrated, predominantly, in various phases of a multi-component food system. As a result of this, each of them loses the capacity to perform structural functions throughout the entire food system. On the contrary, complexing proteins and polysaccharides may lead to formation of both soluble and insoluble complexes which may differ greatly in their properties from the properties of individual macromolecular reactants. The soluble complexes may be considered to be a new type of biopolymers (with different functional properties) which have the capacity to perform structural functions throughout the entire system. In view of this, there were undertaken, in recent years, systematic studies of functional properties of proteins and polysaccharides, including study of their solubility, gelation, emulsifying and foam-stabilizing capacities in solutions of individual macromolecular substances and in mixtures of them and also in actual multi-component food systems.

Especially interesting results were obtained in studies of phenomena of limited thermodynamic compatibility of proteins with other proteins and of proteins with polysaccharides and also of the conditions of formation and the functional properties of complexes of proteins and polysaccharides. At the same time, there appear many physico-chemical phenomena which are of fundamental importance in reprocessing protein into new forms of food and which have been used in attempts to solve problems in the technology of

production of new food products. These include, for example, uneven effects when complexing proteins and anionic polysaccharides which are important components of food products. These effects are evident in the dependence of the structure and properties of complexes, especially their solubility, on production conditions. They make it possible to produce both completely insoluble complexes and also concentrated solutions of soluble complexes. The first effects are important for separation of the protein or polysaccharide from dilute solutions and the second effects are important for regulation of properties of the protein during the reprocessing of it into food. In addition to this, it was found that complexes of proteins and polysaccharides have the capacity to form gels which are resistant to heating under conditions during which individual microreactants generally do not have the capacity for gel formation. It was found also that, as a result of denaturation of proteins in the compound of complexes and anionic polysaccharides, the stability of the complexes increases in a wide range of pH and ionic force of the medium and it was also established that soluble complexes of anionic polysaccharides have higher surface activity than do free proteins. These results can be applied practically during production of concentrated food emulsions, stabilized by complexes of milk complexes and apple pectin. These emulsions, produced on the basis of milk protein and animal fat, possess thixotropic sausage-like properties. They can replace 30 percent of the meat used to produce sausage products, making it possible to increase both production volume and savings in production and also making it possible to improve the quality of the food products produced. High quality products may be produced, in this case, even when including natural meat sausages with poor functional qualities.

Now we shall present examples of practical use of the phenomenon of limited thermodynamic compatibility of biopolymers. Sufficiently concentrated systems containing mixtures of proteins or of proteins and polysaccharides are separated into layers under conditions which lead to suppression of complex-formation of these macromolecular substances, which is seen, for example, in mixtures of proteins and polysaccharides when their overall concentration is nearly 4 percent and higher and when the salt concentration in the system is higher than 0.2-0.5 M/l. It is essential that the phase equilibrium in these systems is established, basically, at the expense of transfer of the water from one phase into another. At the same time, one of the phases (predominantly containing protein) is concentrated and the other (polysaccharide phase) is diluted. This method has been used practically for highly-productive concentration of solutions of proteins under soft conditions. Of course the process of concentrating protein solutions while mixing them in polysaccharide solutions under conditions which are responsible for the limited thermodynamic compatibility of these macromolecular substances may have practical significance only if there is the possibility of effective practical use of dilute polysaccharide solutions (which are used widely in the confectioner's industry) or if regeneration of the polysaccharide from the dilute solution and its repeated use to concentrate new batches of the protein solution are possible. Regeneration of the polysaccharide is achieved by precipitating it in the form of an insoluble complex with a relatively small amount of protein and returning it

into the process. This new method of concentrating protein solutions is called membraneless osmosis. It is being mastered by industry for concentration of protein of defatted milk with the aid of apple pectin. With a concentration of more than 1 percent, there is rapid (within 1-2 minutes) concentration of proteins of the defatted milk from 3 percent up to 30 percent concentration. Liquid phases of the protein solution and the polysaccharide solution are divided by settling or by separation.

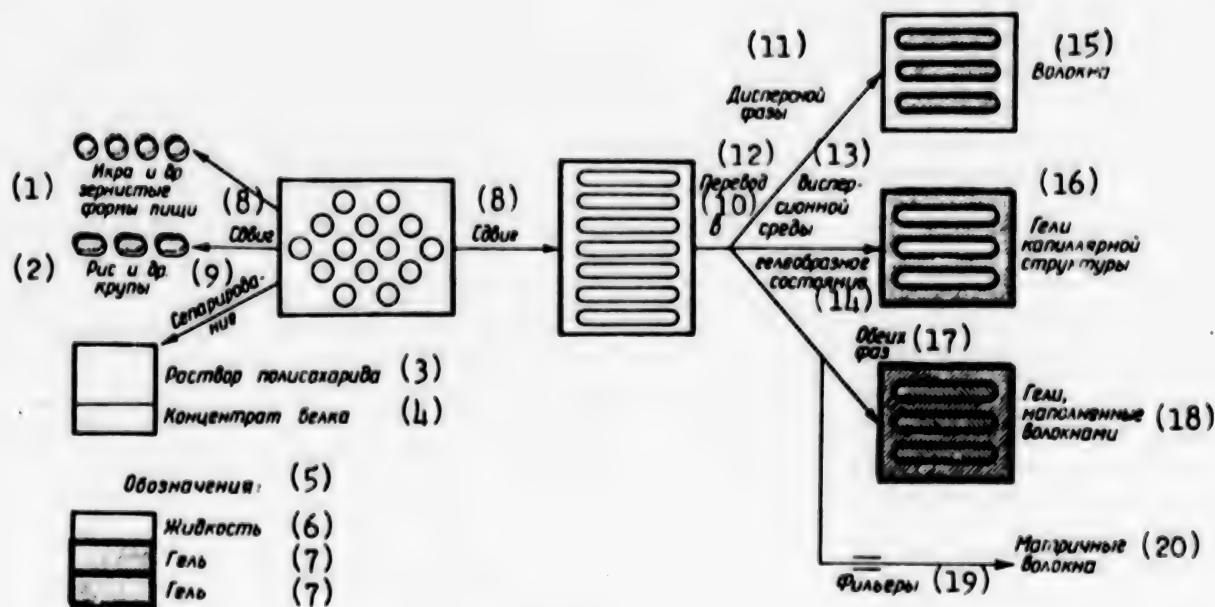
Another process, based on limited thermodynamic compatibility of proteins and polysaccharides, involves production of food protein fibers without a funnel. In the process of non-funnel spinning, just as in funnel spinning, forming nozzles are used to produce liquid jets of the spinning system. During funnel spinning, each opening of the funnel ensures production of an individual monofiber. On the contrary, during non-funnel spinning, each forming hole provides production of a great number of fibers, i.e., a bundle of oriented fibers. In other words, during non-funnel spinning, each hole works just as a funnel as a whole in the ordinary case. Such an effect is ensured because of the conversion of the two-phase liquid systems and it is found to be possible to produce fibers differing in structure and filamentary non-cloth materials and also to regulate the properties of fibers. We shall explain why these things are possible.

Two-phase systems, produced by mixing solutions of proteins with solutions of other proteins or with polysaccharides, are a "water in water" type of emulsion. Generally, the following versions (see figure) of converting such protein-containing emulsions into food products are possible.

In the first place, in a flow such as that which occurs during passage of a two-phase liquid system through a forming nozzle, the liquid dispersed particles may be deformed and assume the form of liquid filaments. These filaments (liquid cylinders) may be converted into a gel-like state with formation of thin, short fibers. If the concentration of dispersed particles in a system is sufficiently high, the interaction (coalescence) of liquid particles deformed in the flow make it possible to produce fibers of infinite length or non-fabric filamentary materials which imitate meat products in macrostructure and consistency. On the contrary, if deformation of the liquid particles in a flow is small or completely absent, we obtain granules of one or another form, which imitate berries or grains of rice, for example.

In the second place, if the dispersed liquid particles of a two-phase system are deformed in a flow and pass, in the gel-form state, into a continuous phase (i.e., a dispersion medium) of the system, gels filled with oriented liquid filaments are formed. Such gels are called gels of capillary structure. At high degrees of filling of the gel by liquid cylinders situated between them, the continuous phase of the gel consists of filaments but these filaments have a cylindrical form.

Of course, if the dispersed particles are deformed in the flow and both phases of the system are converted into a gel-like state, gels filled with oriented filaments are formed. They possess significant anisotropic



mechanical and other physico-chemical properties just as gels of capillary structure do. An interesting property of such gels is their capacity to form fibrils, i.e., to split into filaments upon deformation. The breakup of these gels into fibers, when they are chewed, creates a sensation of non-uniformity which is characteristic of meat products.

Thus, the use of two-phase liquid systems of different composition and of methods of generating their flow and fixing the structure makes it possible to produce various protein textures and analogs of different food products. Thus, two-phase liquid systems containing milk products and pectin are used to produce protein filaments without use of a funnel and this process has been used to produce compound meat products. These fibers are resistant to hydrothermic effects (cooking) which, evidently, is caused partly by the triple casein-calcium ions-pectin complexes. It is important that conversion of two-phase liquid systems into fibers may be performed under softer conditions and on less complex apparatus than is the case during ordinary funnel spinning. In addition to this, it makes it possible to convert mixtures of proteins and to widely vary the composition, biological value and properties of food protein fibers and to convert various proteins, including those which are not subject to spinning. The latter is due to the fact that the capacity for spinning of emulsions and the properties of the fibers are determined, primarily, by properties of the dispersion medium and the formed systems (with continuous matrix phase).

We also emphasize that protein texturates produced by thermoplastic extrusion and also texturates produced with the use of an additional structurizing nozzle are, in essence, anisotropic gels with capillary structure, forming during gelation in a flow of two-phase systems, the dispersed phase of which consists of deformed bubbles of water vapor or drops of water. The possibility of modelling key physico-chemical processes of texurization and of studying their mechanism (see figure) ensures further improvement in protein conversion methods.

The examples presented show the unusual diversity of physico-chemical phenomena in food products mixtures of a macromolecular nature and also their great importance in converting protein into new forms of food. In addition to this, we point out that selection, as an example, of only one multi-component system containing milk proteins and pectin was done in order to show that all of these phenomena may be observed in one and the same system but under different conditions and that they are realized under actual conditions by isolating and converting proteins which ensures variation of functional properties of the protein and thus predetermines the structure and properties of prepared food items. Actually, as was noted in the system containing milk proteins and pectin, it is possible, depending on conditions of mixing the macromolecular components, to form both insoluble complexes, used to separate protein or pectin from diluted solutions and to produce soluble complexes which may serve as stabilizers of emulsions, foams, gel-formers, structure regulators and rheological properties of a food system. Under conditions of suppression of complex-formation, this system may be separated into layers, spontaneously, with concentration of protein in

one of the phases of the liquid system (membraneless osmosis method). Deformation of liquid dispersed particles in a flow makes it possible to produce a wide range of new food products.

Thus, the examples presented indicate the generality of physico-chemical problems in the area of separation and conversion of protein into food and in the area of production of various new forms of food (such as protein fibers, granules and anisotropic gels, for example) with composition and properties desired. They demonstrate the effectiveness of a general physico-chemical approach to the production of new food products.

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PILOT PLANT STUDIES ON PRODUCTION OF HEMICELLULOSE HYDROLYSATES FOR INDUSTRIAL-SCALE CULTIVATION OF YEAST

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 6, 1985  
pp 5-7

KOROLKOV, I. I., LEVANOVA, V. P., YABLOCHKINA, S. P., BALASHEVICH, I. I.,  
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[Abstract] Trials were conducted on the effectiveness of wood-derived hemicellulose hydrolysates as nutrient medium for commercial yeasts. Hemicellulose hydrolysates obtained by mild hydrolysis at 140-150°C yielded 20% reducing substances after inversion at a pilot plant. Cultivation of industrial yeast strain KIR-5 on the hydrolysate resulted in 20-25% higher yeast yields than on standard nutrient media. The conditions employed consisted of a hydrolysate flow rate of 26-30 m<sup>3</sup>/h for 9 days. These observations indicated that high yeast yields are possible from wood-derived hemicellulose hydrolysates, and that such processing technology should be incorporated into the production of plant-carbohydrate feed.

[91-12172/12955]

UDC 630\*863.1+630\*863.1:662.641

COMBINED HYDROLYTIC PROCESSING OF WOOD BYPRODUCTS AND POORLY DECOMPOSED SURFACE PEAT

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 6, 1985, pp 13-15

NAUMOVA, G. V. and BRATISHKO, R. F., candidates of technical sciences, LOYKO, M. N., engineer, and BELYAVSKAYA, T. D. and RAKHTEYENKO, T. S., junior scientists, Peat Institute, Belorussian SSR Academy of Sciences, KRAYEV, L. N., candidate of technical sciences, and SHAKHANOVA, R. K. and BARINOVA, N.G., senior scientists, All-Union Scientific Research Institute of Hydrolysis, and VAAKS, V. R., engineer

[Abstract] Trials were conducted on the effectiveness of combined hydrolysates derived from wood and peat in supporting growth of commercial yeast. Studies with hydrolysates derived from wood (80-90%) and poorly decomposed surface peat (10-20%) yielded yeast harvests 6-11% greater in terms of reducing substances than obtained with processed wood hydrolysate alone. Yeasts grown on wood hydrolysate contained 50.3% protein, while those obtained from the combined hydrolysate contained 55.1% protein, i.e., a 4.8% improvement in terms of protein concentration. References 5 (Russian)  
[91-12172/12955]

UDC 66.047.58.664.834.25

## ROLLER DRUM DRYER FOR POTATO PUREE AND OTHER PASTRY MATERIALS

Moscow KHMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 9, Sep 85 pp 11-12

KORYAGIN, A. A., candidate of technical sciences, MAMISTOV, V. V. and TOKAREV, V. V., engineers

[Abstract] A new roller-type drum dryer, designated VN2-5NU-01, has been designed and put into mass production for operation in food production plants. Schematic cross-section and other technical details are provided, in particular as it is used for the drying of potato puree. In the case of potato puree the dryer has been found effective in reducing the moisture content from 78-80% to 10-13%, producing a film 0.1-0.15 mm thick. The machine described has a controllable rpm of 2-8, a working surface area of 28.7 m<sup>2</sup>, and an operating efficiency of 2250 kg/h of the potato puree feed. VN2-5NU-01 has also found application in other branches of the food industry (juices, yeasts, etc.), as well as in the microbiological (enzymes, protein concentrates, etc.) and chemical (pigments, colorants, etc.) industries. Figures 1.

[98-12172/12955]

UDC 533.15:661.94.664.833

## PERMEATION OF OZONE THROUGH PLANT TISSUE SECTIONS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 284, No 5, 1985 (manuscript received 15 Jan 85) pp 1167-1170

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[Abstract] Experiments were conducted with potato and carrot section to obtain quantitative data on the permeation of ozone, in view of the potential use of ozone for plant preservation and as a fungicide. The data were compared with similar information derived for CO<sub>2</sub> since the molecular dimensions of O<sub>3</sub> and CO<sub>2</sub> are similar, but the latter has the advantage in such studies of being chemically inert. The diffusion constants for CO<sub>2</sub> ranged from  $4 \times 10^{-9}$  cm<sup>2</sup>/sec for potato cortical tissue to  $10^{-6}$  cm<sup>2</sup>/sec for the carrot medullary tissue. Additional measurements revealed that the rate of permeation across a 100  $\mu$ m section was 10- (potato medullary tissue) to more than 20,000-fold (carrot medullary tissue) faster for CO<sub>2</sub> than for O<sub>3</sub>. The depth to which O<sub>3</sub> penetrated into the tissues ranged from a maximum of 50  $\mu$ m for the carrot cortex to 700  $\mu$ m for the carrot medulla. The process of O<sub>3</sub> permeation into the plant tissue can be regarded as a diffusion process complicated by ozone's chemical reactivity with a variety of tissue groups, e.g., -C=C-, -OH, -NH, etc. Figures 2; references 5: 4 Russian, 1 Western.

[99-12172/12955]

INORGANIC COMPOUNDS

UDC 548.5

ALUMINUM ORTHOPHOSPHATE AND BASIC POLYPHOSPHATE PRODUCTION UNDER HYDROTHERMAL CONDITIONS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 284, No 4, 1985  
(manuscript received 2 Nov 84) pp 881-885

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[Abstract] Berlinite ( $AlPO_4$ ) was synthesized by published hydrothermal methods and by crystallization from metastable aluminum phosphate glasses. An aluminum metaphosphate glass as a starting material provided improved solubility in phosphoric acid because of the lack of a long-range crystalline structure. The aluminum metaphosphate is probably hydrolyzed to  $Al(H_2PO_4)_3$ , which under proper conditions can then crystallize out as berlinitite, with orthophosphoric acid left in solution. Crystallization at 300°C was studied over a 360 hr period from various media, including 2, 4 and 6% aqueous HCl. These gave crystals with infrared spectra corresponding to berlinitite, although crystals from the 2% solution showed some extraneous refraction bands indicative of imperfect lattice growth. Crystals grown in  $HNO_3$ , KF, and NaOH at 8% concentrations also showed extraneous refractions, with crystals from the caustic soda containing a significant number of -OH groups. Crystals from 0.5 to 5 mm of basic aluminum polyphosphate-- $Al[P_3O_8]OH_2$ --were also formed, using a temperature gradient to provide proper supersaturation in the crystal growth zone. Infrared spectroscopy of these finely powdered crystals indicated an endothermal effect in the region 545-620°C, with an accompanying weight loss of 9-10% and a transformation into aluminum metaphosphate. Consequently, crystals of basic aluminum polyphosphate were used as feed for the growth of berlinitite crystals. Figures 4; references 9: 4 Russian, 5 Western.

[55-12672/12955]

NITROGEN COMPOUNDS

BRIEFS

ADDITIONAL AMMONIA PRODUCED--(TASS, Grodno)--The capacity of the flagship of Belorussian chemistry--the Grodno Azot Production Association imeni S. O. Prikitskiy--is increasing at a rapid rate. A large-tonnage unit for producing ammonia which went into operation at the beginning of the year was brought up to the projected level here ahead of schedule. Because of this, more than 13,000 tons of additional valuable output has been produced. [Text] [Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 19 Oct 85 p 1] 12255

CSO: 1841/67

ORGANOMETALLIC COMPOUNDS

UDC 543.544:546.831

SYNTHESIS, PROPERTIES AND ANALYTIC USE OF SILICA CHEMICALLY MODIFIED WITH HYDROXAMIC ACID

Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 40, No 8, Aug 85  
(manuscript received 17 Oct 84) pp 1387-1393

VERTINSKAYA, T. E., KUDRYAVTSEV, G. V., TIKHOMIROVA, T. I. and FADEYEVA, V. I., Moscow State University imeni M. V. Lomonosov

[Abstract] A silica-based adsorbent was prepared by the reaction of hydroxylated silica with  $\text{Cl}_3\text{Si}(\text{CH}_2)_2\text{COOCH}_3$  and of the resultant product with  $\text{NH}_2\text{OH}$  in methanol at pH 8.0. The adsorbent was subsequently utilized for chemisorptive concentration and separation of Sc(III) ions and group IVA elements (Ti, Zr, Hf, Th), based on the high selectivity of the hydroxamic group for these ions and tolerance of acidity (0.1-4 M  $\text{H}^+$ ). Effective separation of Zr and Hf, on the one hand, from Fe(III), Sc and Th, on the other, was based on differences in the acidity promoting maximal absorption. Quantitative separation of Zr-Sc, Zr-Fe and Zr-Th pairs was obtained with 10<sup>4</sup>-fold excess of Sc, Fe(III) or Th. Chromatographic column separation was predicated on formation of a complex between the metal ions and the grafted hydroxamic groups. The coefficients of concentrations approached 100 in the case of Sc, Zr and Th. Figures 3; references 29: 20 Russian, 9 Western.  
[048 12172/12955]

UDC 541.127+546.562+547.496.2

KINETICS AND FORMATION MECHANISMS OF Cu(II) DITHIOCARBAMATES IN ACETONITRILE

Kiev UKRAINSKIY KHMICHESKIY ZHURNAL in Russian Vol 51, No 8, 1985  
(manuscript received 16 Apr 84) pp 787-791

MALETIN, Yu. A., VERKHOVLYUK, T. V. and SHEKA, I. A., Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Spectrophotometric studies were conducted on the synthesis of copper(II) bis-diethyldithiocarbamate obtained in 95% yield in a system of

copper acetate, diethyldibenzylamine, and carbon disulfide in acetonitrile. Analysis of the kinetics demonstrated that the reaction was second order in amine and first order in carbon disulfide. The rate constants of the reaction were increased by addition of pyridine and decreased by an increase in the reaction temperature or the concentration of copper acetate, as well as by replacement of diethyl- by dibenzylamine. The kinetic data were in accord with a reaction mechanism involving an initial stage of complex formation with amine  $\rightarrow$  carbon disulfide charge transfer. Subsequently, the initial complex reacts with a second molecule of the amine in a rate limiting step to give the dithiocarbamate anion, and the latter gives rise to a firm complex with copper. Figures 4; references 6: 2 Russian, 4 Western.  
[045-12172/12955]

UDC 541.49+541.127

#### EFFECT OF LIGAND SUBSTITUENTS ON PROPERTIES OF MACROCYCLIC ZINC COMPLEXES

Kiev TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA in Russian Vol 21, No 4, 1985 (manuscript received 3 Jul 84) pp 424-431

PAVLISHCHUK, V. V., RYBAK-AKIMOVA, Ye. V. and YATSIMIRSKIY, K. B., Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, UkrSSR Academy of Sciences, Kiev

[Abstract] Replacement of a central ion in macrocyclic complex compounds is of interest in coordination and biocoordination chemistry, yet their mechanism of formation and reaction kinetics have been poorly studied. In the present work the effect of substituents in the macrocycle on replacement kinetics of Zn ions by Cu ions was investigated on 14-member tetraazamacrocyclic ligands (L). The distribution of electronic density in the coordination node of zinc complexes with macrocyclic compounds was studied by X-ray electronic spectra using the ESCA-3 "Vacuum Generator" unit. It was established that the number of methyl substituents and their location on the macrocycle has practically no effect on nitrogen and zinc atomic orbital overlap nor on the degree of electronic density transfer from donor atoms of the ligands to the metal. In the pH range 4-6, the reaction rates of  $ZnL^{2+}$  with  $Cu^{2+}$  do not depend on pH. The reaction rates of the replacement of  $Zn^{2+}$  by  $Cu^{2+}$  are described by second order kinetic equation: first order in respect to  $ZnL^{2+}$  and first order in respect to  $Cu^{2+}$ . Energy values and enthalpy of activation were practically identical for all reactions studied. Figures 3; references 19: 6 Russian (1 by Western authors), 13 Western.  
[53-7813/12955]

ORGANOPHOSPHORUS COMPOUNDS

UDC 548.737

STRUCTURE OF CRYSTALLINE P-TRIMETHYLSILYL-C-DIMETHYLAMINO-C-DIETHYLAMINOMETHYLENEPHOSPHINE

Kiev UKRAINSKIY KHMICHESKIY ZHURNAL in Russian Vol 51, No 8, 1985  
(manuscript received 6 Apr 84) pp 868-874

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[Abstract] X-ray structural analysis was conducted on a novel bicoordinated phosphorus compound, P-trimethylsilyl-C-dimethylamino-C-diethylaminomethylene-phosphine (I), with the data for I compared with similar information on acyclic phospha-alkenes previously synthesized. At room temperature I exists in the liquid state ( $T_m$  ca.  $-10^\circ\text{C}$ ). X-ray data for the monoclinic crystals of I prepared at  $-120^\circ\text{C}$  showed  $a = 9.370 \text{ \AA}$ ,  $b = 7.602 \text{ \AA}$ ,  $c = 1.9.84 \text{ \AA}$ ,  $\beta = 90.73^\circ$ ,  $d = 1.09 \text{ g/cm}^3$ ,  $Z = 4$ , and  $P2_1/c$  spatial group. Bond lengths in I were calculated at  $\text{P-Si} = 2.236 \text{ \AA}$ ,  $\text{P=C} = 1.761 \text{ \AA}$ , and  $\text{C-N} 1.360$  and  $1.388 \text{ \AA}$ , with the  $\text{SiPC}$  angle at  $106.16^\circ$ . The relative elongation of the  $\text{P=C}$  bond and the shorter  $\text{C-N}$  bonds in I in comparison with standard values indicate electronic delocalization in the  $\text{N-C-P}$  triad with the involvement of both  $\text{N}$  atoms. Figures 1; references 26: 5 Russian, 21 Western.  
[045-12172/12955]

UPGRADING, SUITABLE ASSORTMENT OF AGRICULTURAL MACHINES CALLED FOR

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 18 Oct 85 p 2

[Article by Yu. Veretennikov, chief engineer of the Soyuzselkhozkhimiya Association of the USSR Ministry of Agriculture: "Captive to Conventional Layouts"]

[Text] Moving the economy onto the fast track of development, getting it to a higher level of organization and effectiveness--the importance of these program tasks was particularly emphasized at the just-concluded CPSU Central Committee Plenum. They have a most direct relationship to intensive technologies of farming.

Every year, more and more chemical compounds are used on the fields to protect plants from weeds, pests, and disease. But it must be acknowledged that the level and quality of chemical treatment currently does not correspond to the expanded requirements of agricultural production.

In the countryside, automatic tanks, water dispensers, and other more or less suitable equipment is being adapted for these purposes. There are tens of thousands of these patchwork devices in kolkhozes and sovkhozes. It is better not to talk about their technical level and, accordingly, quality. It follows that you don't regulate the dosing of solutions here, since the application frequently goes according to the principle "sometimes thick, sometimes thin." The results are visible to the naked eye: where it is thin the yield is poor, where it is thick there are losses of pesticides and plants are burned.

It is true that farms are receiving special mechanisms manufactured by plants. The Lvovkhimselkhozmash Association is producing 20,000 sprayers per year. But these are fan-driven mechanisms, intended mainly for orchards. They, like the other available devices, also must be adapted for fields, which of course does not produce the desired results. It is true that for fields there is what is known as boom sprayers, but these do not make any difference, since the demand for them is only being satisfied by 12 percent.

A long time ago we asked the Ministry of Agricultural Machine Building, and the Lvov machine builders directly, to give us field machines instead of orchard ones. After all, the countryside does not have as many orchards as it has equipment being manufactured for them: the demand is not 20,000 but only 7,000 per year. The machine builders continue to have it their own way.

That's right--production aside, there is no wish to break up the structure. And a "trifle" such as the needs of consumers, by all appearances, does not worry them much.

Meanwhile, not only the quantity of the Lvov equipment but also its quality leaves something to be desired. The field sprayers do not meet modern requirements in the width of the area covered, tank capacity, and reliability of work as a whole. The tanks are covered with a paint which flakes off and clogs up the sprayers. And the sprayers themselves, alas, do not ensure precision of dosing. What kind of guaranteed yield can we talk about here?

Speaking of equipment for applying pesticides, we mustn't forget to mention mixers. The situation with them is no better than that with their "colleagues." Here too the kolkhoz members are forced to construct home-made solution units, because these were forgotten when the original aggregates were supplied. Because of the absence of special mechanisms, dosing of toxic chemicals is sometimes carried out using an ordinary pail. And who would have thought that the density of many chemical substances is nowhere near equal to the density of water? That in a 10-liter pail a solution of chlorophos would be not 10 but 16 kilograms?

Because of the unsatisfactory work of machine builders, mixers must be purchased abroad. Not only that, they cost a pretty penny and by no means every farm can afford them. The imported equipment is also unsatisfactory for farms because it is different-colored and not universal. Here one brand, here another--no system can be discerned, and this, naturally, makes it difficult to use them.

Now I would like to dwell more thoroughly on pesticide consumption. I can boldly assert that the quantities of them applied to a hectare are 1.5-2, sometimes even three, times greater than necessary. Such losses of chemical protection work, in rapidly growing volumes, reduce to nothing the efforts of the state to increase the production of these compounds. We were already convinced that not only homemade kolkhoz equipment but also industrial equipment (because of its low quality and technical level) applies plant protection agents very wastefully. Especially from airplanes and helicopters, when only an insignificant portion of the substances falls onto the plants and the remaining portion pollutes the environment. But here much depends not only on the machines but also on the level of scientific research in this field.

The technology of plant treatment is poorly substantiated and also contradictory. For about 20 years scientists of the All-Union Institute of Plant Protection have been studying these questions, but even so, there have been few advances, because the advanced equipment cannot get to agriculture. Why, for example, are 300 liters per hectare of solution applied in treating young crops with one type of sprayer, and only 50 liters with another? Moreover, in the second case, up to 90 percent of the compound is lost. Why is this quantity of expensive pesticides released into the wind to create ecological problems? It is time at last to develop absolutely precise normatives of pesticide application, in order to put an end to waste in this matter. Incidentally, the strictness of norms will force machine builders, in their turn, to tighten up standards.

In January of this year, the USSR Council of Ministers Presidium Commission on Questions of the Agroindustrial Complex, examining the state of affairs in the production of new machines for applying chemical compounds, ordered the Ministry of Agricultural Machine Building to take immediate steps in this direction. In particular, to increase the output of field sprayers by cutting back on orchard sprayers, improve their quality, and supply farms with mixers. As is characteristic, the base for such work is as follows: mixers and universal sprayers are to be developed of a level which surpasses the best foreign examples. (Incidentally, mixers were recommended for production as early as 1978.) But despite the conclusions of the commission and a number of other instructions the Ministry of Agricultural Machine Building continues to avoid resolving long-standing problems. Letters come to the leadership of this ministry and remain unanswered. And if there are replies--they are usually signed by Deputy Minister G. Kirichenko--they are not very comforting: there are not enough capacities.

This traditional argument does not sound very serious. Here is a simple calculation: if production of second-generation equipment is set up for the field, then, keeping the output of machines at the same level, we almost double their productivity! There is still another solution to the situation--standardizing equipment. Why is it that sprayers manufactured in the same enterprise in Tashkent are not standardized with the Lvov sprayers? There are no reasonable arguments for this but the situation is not being changed.

Meanwhile, with only a thousand new machines, by 1986 agriculture could work out economical methods of treating crops, and introduce low-volume spraying of perennial crops to reduce toxic compounds by 25 percent, increasing labor productivity by 25-30 percent. By treating orchards and vineyards alone using the advanced method, the yearly savings of pesticides would be over 100,000 tons. And what possibilities would open up for resolving the economical problem, for organizing the production of an assortment of scarce compounds in economical capacities of the chemical industry!

How can momentum be gathered as quickly as possible? In my view, it is necessary to work out a goal-oriented integrated program of projects to convert agricultural production to new advanced technology with reduced norms of pesticide consumption. In addition, the State All-Union Standard should be reexamined which establishes the order of developing the above-mentioned equipment and installing it in production. The point is, it permits a great deal of interdepartmental differences of opinion between the supplier and the consumer by imprecisely defining the functions of each of them. Until these differences are regulated, we specialists of the Ministry of Agriculture will not be able to fully exercise the rights of a main consumer to have an influence on its production.

For example, certification of machines according to quality categories is frequently carried out without our participation. Representatives of our ministry are not involved in approving quality cards and the technical stipulations on the items manufactured. We are also excluded from participating in the development of measures to eliminate shortcomings of the machines. The State Committee for Standards should impose order in this important matter, and first of all, order industrial ministries and departments to coordinate all normative-technical documentation with us.

In short, it is time to shake off inertia and give up the old systems, in order to make a radical turn toward intensity and quality in the 12th Five-Year Plan.

12255  
CSO: 1841/67

UDC 62-52.001.8

SOME METHODOLOGICAL PROBLEMS IN DESIGNING CONTROL SYSTEMS FOR CHEMICAL ENGINEERING PROCESSES

Kiev KHMICHESKAYA TEKHOLOGIYA in Russian No 4, Jul-Aug 85 (manuscript submitted 26 Nov 84), pp 48-52

[Article by P. V. Kostogryz: "Some Methodological Problems in Designing Control Systems for Chemical Engineering Processes"]

[Text] One of the crucial factors in increasing the productivity of social labor is the automation of production. The intensive growth in the technical level of modern manufacturing, specialization and concentration, and creation of new low- and no-waste technology requires improving existing control systems and creating new, more effective control systems that satisfy current requirements. If the simplest tasks for stabilizing the individual parameters of the objects were performed at an earlier stage of creating control systems, then the present requirements involve the creation of effective and flexible optimal control systems for complicated production processes. The fulfillment of this task rests on automatic process control systems (ASUTP), which must serve as the basis for the creation and functioning of higher-level automated control systems (ASU).

The entire control system, including the ASUTP, must provide qualitative control or optimal control of the process (production system), be stable and effective, and perform three basic tasks:

- gather and transmit information about the controlled object;
- process the information;
- transmit control actions to the controlled object [1].

Despite the similarity of tasks performed, the methods of designing stabilization systems laid down in automatic control theory (TAR) differed somewhat, including selection of the structure and principles of performing individual control tasks for various processes and production systems, with an increase in the requirements on control systems that were continually expanded and improved. It is important to note that the development of the principles of designing SAU [automatic control systems] and improvements in studying them in dynamic models--taking into account the features of the objects, automatic equipment, and operating conditions, as well as the use of the structural

approach to system synthesis--made it possible to establish the type of controlling interactions and the merit of introducing leading or cross feedback for more complicated objects and, most important, to reveal the physical nature of phenomena which lie at the foundation of designing control systems [2] and to create efficient and accurate systems to control quite complicated objects. The systems have become more complex. For example, systems with a variable structure, multiple connected control, etc. [3-6] are complex not only in development, but also in set-up and operation; they require the use of iterative, probability, and other types of analysis, synthesis, and calculation; as well as great expenditures in time and highly qualified specialists [7], but basically are capable of performing only tasks of parameter stabilization. Systems with broader functional capabilities, automatic process control systems (ASUTP), need to be created for optimal control.

Cybernetics--the science concerned with general laws of control and communication in organized systems--is the basis for creating ASUTP [8]. The existence of the powerful body of mathematics of cybernetics, the methods that have been developed for designing SAR [automatic control systems], and the computer complexes that have been perfected exposed the wide-ranging possibilities not only for formulating and studying the general principles of production processes in mathematical models, but also for creating the ASUTP of the most complicated production complexes and studying them by computer. Previously, methods of design have been created; experience in developing and incorporating centralized ASUTP has been accumulated, including direct digital control for various classes of chemical engineering processes [9-15]; the difficulties have been ascertained; and the prospects for developing them have been determined. For example, the diversity of types of real-time production processes, whose complexity is commensurate with a controlled system; the types of possible models of the processes (more than ten attributes); the criteria used and solution methods; the conditions for using models; etc. complicate not only the selection of the development alternatives, which can be in the thousands, but also the creation of the systems themselves [2]. Therefore, the "standardization" of ASUTP, the "universalization" of software for objects of different natures, and the creation of adaptive systems with an identifier in the feedback circuit (ASI) for different types of production processes have been proposed [2]. However, when creating such systems, it should be taken into account that the simple, centralized ASUTPs being developed for application to a specific process are extremely complex and insufficiently reliable. This, primarily, is associated with the complexity and insufficient reliability of the mathematical models of many processes and the control algorithms based on these models that have been created; with the absence or low reliability of equipment to measure the basic parameters, most frequently quantitative indicators of the development of the process, without which the normal functioning of the system is made more difficult, and at times even impossible [13, 16]. Apparently, therefore, only the data portions of centralized ASUTPs are incorporated into production [12]. It is important to mention here, that when the mathematical description of an object is obtained by known methods, often the internal structure is not investigated but the connections between input and output parameters are modeled, assuming that the relationships obtained are

sufficient for the design and functioning of ASUTP [14]. However, models of processes obtained in this way are difficult to analyze and interpret, and they do not reveal the characteristic features of the production process, which experience shows can be successfully used to significantly simplify the control system created. In fact, it is known [17] that without a thorough knowledge of the production process it is difficult, sometimes impossible, to create or even design a control system in a qualified manner, which could be considered properties of the production process for the purpose of ensuring its optimal design. We will show this using the example of creating a system for optimal control of a block of pyrolysis furnaces (plant).

Three tasks must be performed for optimal control of the pyrolysis furnace block (plant):

- optimal control of the temperature regime in each of the six to nine furnaces;
- optimum distribution of loading between the operating furnaces, taking into account the nonstationary behavior of the process (coke formation);
- maintenance of the optimal (specified) productivity of the plant.

The main difficulties in performing these tasks are primarily associated with the presence of a constant shift in the optimum pyrolysis temperature, caused by changes in the consumption and composition of the feedstock, coking of the pipe still coil, and changes in other parameters of the process, as well as by the lack of measurement of the quantitative indices, i.e., yield of target product (ethylene, propylene) and by-products from the feedstock. Centralized ASUTP [16, 18, 19] use methods for sampling and comparing results in three and more stages when determining the optimal pyrolysis temperature, and a repeat sampling of the alternatives at the stage of determining and establishing loadings in the operating furnaces, i.e., the distribution of loading among furnaces. The functional algorithms for such systems are based on complicated mathematical methods (linear and dynamic programming, factor planning, active adaptation, etc.), significantly simplified mathematical models (the universal model of pyrolysis may have up to 1,000 kinetic equations), and assume the presence of complete information about the process, which is practically impossible to obtain: there are no sensors for operational changes in the quantitative indices of the process. The presence of operational changes in the qualitative indices, i.e., the content of pyrolysis products in the pyrogas (% vol.) is insufficient even for calculating the latter: intermediate parameters, for example, gas formation and octane number (during cracking), also impossible to directly measure, are required. Then, special mathematical models are developed to determine them [13, 16], using indirect operationally measured parameters. However, even this does not substantially solve the problem, since the spread of indicators calculated in this way often is equal to, or exceeds, the optimal mode search zone and complicates the system. Despite the substantial simplification, including replacement of the model of a multiple-flow furnace with an equiva-

lent model of a single furnace, the systems remain complex. For example, there are 800 functional parameters in the EP-300 ASUTP.

One of the practicable ways of simplifying the systems may be to use the hierarchy concept, widely used in complex systems at higher levels [20, 21]. However, this is not used when creating ASUTP, because the scale of tasks here is not large, and the breakdown of the production process by known methodology--if it is even possible--does not have any special advantages in the plan to simplify the system and reduce information flows and instrumentation. Nevertheless, certain ASUTP is termed hierachic, belonging to the lower levels of the hierarchy of information systems or parameter stabilization systems, whose regulator settings are changed from a central computer [12, 13, 16].

The hierachic system of optimal automatic process control (ISAUTP) at each level must be closed, via external or internal ties; autonomously perform optimum automatic control of the level; and each successive level must correct the conditions to the optimum, as necessary, from the previous level to achieve optimal control of the system as a whole. The most expedient link between levels, as we have established, is the criterion link. Criteria (in isolated cases they could be the basic parameters -- indicators of the course of the process) stem from, or coincide with, the criterion of the degree of optimization of the entire system (upper level). There has been no experience in creating such systems in our country or abroad. Therefore, the main efforts have been directed to the search for new approaches, not only to designing a system, but also to studying the production process with the aim of disclosing the characteristic interrelationships of parameters which would serve as the basis for creation of the system.

The method that has been developed involved comprehensive research of the industrial pyrolysis of benzene and hydrocarbon mixtures over a broad range of changes in composition of the feedstock, and was based on the use of known classical methods, methods of planning an active-passive experiment, mathematical statistics, numerical modeling, and a number of other methods, as well as several examples of processing and presenting experimental data and results obtained. Such an approach made it possible to set up and study the previously unencountered dependence of indicators that integrally and sufficiently fully characterize pyrolysis conditions (simple and complex relationship coefficients -- PKS and SKS, respectively), and the nonstationary behavior of the process (pressure differential caused by coking of the pipe still coil  $\Delta P_c$ ) on the basic parameters of the process (plant). They formed the basis of the development of new means of control, including even the nonstationary processes [22, 24].

Thus, a control method was developed, based on the relationship principle, to perform the first task when there is insufficient information on the course of the process, i.e., when only the content of the target products (ethylene, propylene) and by-products (propane, etc.) in the pyrolysis gas are measured. During development of the method, it was assumed that the progress of any process is always determined by two objectively existing and oppositely directed trends, causing an improvement or deterioration of the end results

of the process. The nature of their change depends on the degree of influence on each of them of the specific combination of input parameters and internal characteristics. Then, the most obvious, objective, and accurate evaluation of the process' course is possible according to indicators, whose nature of change would correspond to changes of the specified trend, because such indicators integrally and most fully would characterize the condition of the course of the process. However, the use of two such indicators is not efficient, since changes in the input parameters and internal characteristics can cause certain combinations of changes in these pairs of indicators, which would complicate selection of the optimum modes. It is advantageous to have one indicator that would provide the most complete evaluation of conditions of process flow. Research has shown that the relationship of conflicting indicators, specified above, responds to these requirements. This stems from the rule we obtained [24], showing that the relationship of the partial derivatives of the output of ethylene and propylene from the feedstock at the optimum pyrolysis temperature is determined by the size of their ratio, i.e., the relationship of two output indicators (parameters), oppositely changing in the control zone. From this, it follows that it is possible to determine the optimum (corresponding to the given relationship) temperature according to the specified (optimum) value of the relationship, and by automatically controlling the optimum temperature, to maintain the specified (optimum) relationship, i.e., to maintain the specified (optimum) pyrolysis regimes such that the size of the ratio is specified according to the matrix of optimal values of the process control criterion selected. For other processes, not less than two output parameters, each of which would reflect the character of change of one of the specified trends in the process control zone, are selected as the conflicting indicators, for example: in fractional distillation, the output of the basic product and by-products; in mechanical crushing, the output of two (three) standard fractions; when cutting metals, the depth and speed of cutting; etc. It is important here only that the selected indicators characterize the progress of the process sufficiently fully, and that an increase in one indicator in the control zone is accompanied by a decrease in the others.

The legitimacy of such an approach has been confirmed by comprehensive research of the industrial pyrolysis of straight-run benzene and hydrocarbon mixtures over a wide range of change in composition and control systems. Thus, it has been established that any--including uncontrollable--disturbances, as well as changes in internal characteristics of the object, cause changes in one--or simultaneously two or more--of the selected conflicting indicators of the process, i.e., any changes in the process cause a deviation in the running values of the relationship. Constancy of not only the size of the ratio of outputs of target (ethylene, propylene) products from the feedstock (% (by weight) and t/hr) are achieved by stabilizing the specified value of the ratio of volumetric concentrations of ethylene to propylene in the pyrogas (simple coefficient of relationship -- PKS), with nearly constant composition of initial raw material, but also constancy in their concentrations and yield from the feedstock, with minimum deviations of concentrations and outputs of by-products (hydrogen, methane, propane, etc.), i.e., the approximate conditions of pyrolysis are achieved. A composition whose potential capabilities significantly differ is widely used to control pyroly-

sis of hydrocarbons. It is necessary to use the complex coefficient of relationship -- SKS. The SKS expresses the ratio of volumetric concentrations of ethylene in the pyrogas to the total propylene and propane. The last indicator (the quality of the raw material in PBF [not expanded] pyrolysis) is multiplied by the coefficient of the permitted zone for scanning the optimum temperature regime, whose range depends on the degree of change of the composition of the feedstock, the criterion of optimization selected, technological limitations, etc. The size of the PKS or SKS is assigned by the results of research and optimization of the process according to the matrix of optimal values of the optimization criterion selected. By changing the size of the PKS or SKS, it is possible to set up ethylene, propylene, or any other mode of pyrolysis, which is necessary in the production situation created. When controlling the process according to the relationship for each given consumption and composition of feedstock--taking into account the possible deviations in process flow conditions caused by any disturbances, including coking of the pipe still coil--the search for and maintenance of the optimum temperature regime is provided according to the optimization criterion selected. The main advantages of the method, from the point of view of automated control, such as for example, the optimal control by qualitative indices (shortage of information) and simplicity of implementing the systems, the increase in sensitivity and decrease in the effect of measurement errors on accuracy of control, etc., are achieved through the efficient use of the characteristic features of the relationship principle, including objective evaluation of process flow according to the accepted criterion, by means of the balanced application of positive and negative results of the effect on the process, and preliminary strengthening of the controlling signal, in which the degree of mutual effect of internal links on the end results of management of the process has been considered.

Experience in development and introduction has shown that ratio control, along with the advantages noted, makes it possible to significantly simplify task performance with optimum distribution of loadings among the equipment, including both nonstationary processes and matching material flows for multiple-flow production, to perform the task of optimal control of processes of varying complexity more concisely and by comparatively simpler means, and can--with serious regard to it--become one of the promising means to perform control tasks for complicated production complexes.

As the basis for performing the second task -- the development of a method for optimum distribution of loadings among operating furnaces -- the characteristic features of the redistribution of material flows during nonstationary behavior of the process and maintenance of optimum productivity of the equipment, depending on the production situation (changes in the loading of subsequent production) were assumed, as well as the known position that the error signal in similar SAR [automatic control system of the regulator type] is not continuous, but discrete [25]. Coking of the pipe still coil gradually deteriorates the operating characteristics of the furnace, and the output of pyrolysis target products and by-products noticeably decreases by the end of the process, especially after 70 to 85% of furnace operation. Complete compensation for deviations in the process flow caused by a change in the temperature regime, even with ratio control, is impossible. The fact

is, the capacity for temperature compensation is limited by the extreme severity of the temperature regime, since coking of the furnace over its life cycle, as has been established, is equivalent to increasing its optimum loading (7.5 t/hr) in a clean furnace by 1.2 t/hr. The furnace is as if it were overloaded, and even a clean surface on the coils could not in this condition transfer the required amount of heat to the flow to maintain the optimum (assigned) pyrolysis conditions at the loading corresponding to its optimum level in a "clean" furnace. Therefore, the proposed control process, for the purpose of maintaining the optimum loading of each operating furnace separately, provides a discrete change (reduction) in furnace loading over its life cycle according to the optimum strategy, i.e., in strict correspondence with the increase in coking of the pipe still coils. To maintain the specified (optimum) productivity of the plant (third task), it provides an even redistribution of running changes of overall loadings of the plant among operating furnaces, taking their condition into account. The discrete size of the change in loading, with the aim of the guaranteed indication of the signal to reduce (increase) it and minimum effect on the change in output (pyrogas composition), is selected at 10 to 20% greater than the stabilization (regulation) circuit dead zone, and the difference between load switching signals must exceed by 10 to 20% the zone of fluctuation of the selected switching parameter caused by allowable deviations in operating modes, taking into account errors in the measurement circuit, to guarantee indication. The switching parameter selected must most completely characterize the process flow conditions. For example, during pyrolysis the pressure differential  $\Delta P_c$  in the greatest coking section of the furnace (radiant section of coil and ZIA [not expanded]), corresponding to a change in hydraulic resistance and caused by coking of the specified segment, was chosen as the indicator of nonstationary behavior.

The methodology for implementing the process involves obtaining the optimum loading change profile for the life cycle of the furnace in loading coordinates -- the switching parameter conforms to the optimization criterion selected, on the basis of which the optimum range of change is determined. In PBF pyrolysis, this is from 7.3 to 6.1 t/hr for a double-flow 7-ton furnace. The obtained range is subdivided into a number of levels with the discreteness specified above. The reference levels of the switching parameter ( $\Delta P_c$ ) are determined by the intersections of the obtained levels of consumption with the optimum loading change profile. These levels are adjusted to ensure longer term operation at higher loadings from among the number of selected levels of the optimum profile, while maintaining the conditions specified above. As a result, the optimum strategy for switching loadings is obtained, expressed as a matrix of optimal values, on the basis of which the levels of pneumatic (electric) signals used in the system for implementing the control process are determined. The signals, proportional to the optimum loading levels (7.3, 7.0, 6.7, 6.4, and 6.1 t/hr) and switching parameters ( $\Delta P_c$  -- 0.15, 0.29, 0.42, and 0.53 atm), are interrelated and can vary from the center signals by loading and switching parameter, respectively. Both center signals are linked to the main controller, designed to maintain the specified (optimum) productivity of the pyrolysis plant (shop).

It is important to note that the proposed process makes it possible, along with the substantial simplification of the system for optimum loading distribution and maintenance of the specified (optimum) productivity of the plant (shop), to strictly control the loading of operating furnaces according to the optimal strategy (the system restricts increasing loading above that specified (optimum) without the compulsory change in the level of switching signals), to constantly monitor the condition of the furnaces during operation and coke burning, to ensure the serviceability of the system in the error zone in control circuits for the main process parameters, etc.

The implementation of the proposed control processes, as research and industrial verifications have shown, makes possible automatic optimization of the pyrolysis process by two basic parameters: pyrolysis temperature and loading. Based on them, a three-level hierachic system for automatic process control (ISAUTP) of a block of pyrolysis furnaces (plant) was developed, capable of performing the three specified tasks by comparatively simple equipment. The lower level is a closed subsystem, on which the ratio principle was established. The subsystem for each given consumption and quality of raw material provides, in conditions of nonstationary behavior and insufficient information on the course of the process, automatic scanning and maintenance of the temperature regime that corresponds to the values of the assigned SKS (PKS) pyrolysis conditions, i.e., to the maximum optimization criterion, for example the output of total target product. The link with the middle level is internal (via a technological process). With the upper level, as needed, it is an external criterion link, according to the ratio criterion, where correction of values is necessary.

The middle level is an open subsystem, based on the proposed method for loading distribution. The link with the upper level is a criterion link by plant productivity, which in essence closes the middle and upper level into a system, with automatic distribution in accordance with the optimum strategy and with adjustment of the raw material loading of operating furnaces. The upper level is a system for automatic determination and maintenance of the optimum loading of the plant by raw material, required to ensure the specified yield of target products (ethylene, propylene). The assignment for producing the latter is generated in the simplest blocks, taking into account the quality of process management and, in a more complicated variation, is generated in a minicomputer that also performs coordination, planning, and other ASU functions.

The method of ISAUTP design involves detailed, comprehensive research of the process and plant as an object of automatic control, using a broad arsenal of classical and other methods for studying the processes and systems, including planning the experiment, mathematical modeling, etc. Obtaining the characteristic relationships between the operating parameters and material flows is important here, as well as determining contradictory indicators that most completely characterize the conditions of process flow and nonstationary behavior. However, owing to the use of new processes, only the final results of the research and optimization of the process, in the form of a matrix of optimal values of general and local criteria, ratio criterion, optimal strategy of changing the leading parameters (indices), etc. are used to im-

plement control in this system. Therefore, the ISAUTP that has been developed favorably differs from centralized ASUTP not only by simplicity and compactness, but also by a one- to two-fold reduction in information flows and equipment, a substantial reduction in expenditures of resources and time to scan the optimum modes, and an increase in accuracy, reliability, etc. This is achieved through the efficient use of the advantages of the ratio principle, criterion method of system design, discrete development of optimum strategies with the minimum possible--but guaranteed--value of control response signals, etc. Certain nonstandard instruments and algorithms, implementing the new control processes, are required for the practical implementation of ISAUTP, in addition to operating systems for stabilizing the main parameters of the process [24, 27, 28].

From that presented above, it follows that the hierarchic principle with all its merits is completely suitable for creating systems for optimal automatic control of production processes and, seriously, can become not only one of the urgent ways to simplify the ASUTP being created, but also to increase its capacity, accuracy, and effectiveness. But for this it is necessary to carry out comprehensive and detailed research of the processes, with the aim of revealing the characteristic features, most objective and operationally changing indicators for evaluating the end results and their link with the criterion of optimality selected, and the most convenient form of displaying the results for the practical realization in the system. The experience in creating ISAUTP for the pyrolysis furnace block (plant) confirms the correctness and practical merit of such an approach, and the methodological approach for it, generally, has been developed.

For many processes, where there already currently exists the possibility for operational measurement of not less than two indicators, oppositely changing in the control zone, objectively and most fully characterizing the conditions of flow of the production process by end results, the proposed methods for control can successfully be used, whose effectiveness, universality, and simplicity of implementation are obvious.

In perspective, the proposed approach, because of its simplicity and universality, can become the basis for constructing standard systems of optimal automatic control of complex production processes and multiple-flow production complexes.

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## PLANNING PRACTICES OF PETROCHEMICAL INDUSTRY CRITICIZED

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 1 Aug p 2

[Article by V. Selyunin, economic reviewer for SOTSIALISTICHESKAYA INDUSTRIYA: "Have the Right Conclusions Been Drawn?"]

[Text] The hall was hushed when Minister V. Fedorov began to speak on the fate of imported equipment which had accumulated in the branch. Everyone understood that at a recent meeting of the CPSU Central Committee on questions concerning accelerating scientific and technological progress the minister was personally subjected to criticism because of the lack of system in the use of purchased equipment. What conclusions were drawn? The speaker gave assurances that measures had been taken, but did not give details.

Now, in petrochemical warehouses lies equipment worth several hundred million rubles. The fate of this wealth is being decided today with the imposition of a long-range plan. It will be a realistic plan and will lead to success. Let us evaluate from this position the construction plan drafts and schedules of works.

The most troubling part of the reserves is the technology, the use of which was not provided for by the plans. Here someone else asks, why incur the costs if you have no intention of using the purchased item either today or in the future? During the course of the current five-year plan the ministry squeezed into the schedule of works hundreds of millions of rubles of such equipment, but much of it still remains unused. These residues are included now in the preliminary draft of the plans for 1986. Was this rational? It should have been, yes.

However, here is the circumstance which puts us on guard. The five-year plan is ending, and the branch has not put into action half of the designated units. Over a period of four years, out of the fifteen facilities for a purchased set of equipment only two were completed on time. In the meantime, 47 new such structures have been begun, and in the next year an additional 18 will be added. Construction sites previously started are being continued. The funds allotted the branches are not unlimited: for 1986, Union Gosplan designated for the ministry a limit of 875 million rubles for building construction and installation. It's necessary to keep within it.

## How do the branch planners act?

Let us look at a volume of schedules of works. The production of higher fatty alcohol in Angarsk has been designated for introduction in 1987. For the next year builders have been allocated three million rubles out of 23 million which must be used. Such an apportionment is death to fulfillment of the plan. In the initial year about six months are used for set-up operations. This means that there remains half a year to fulfill the construction operations valued at 20 million rubles. Can this really be managed?

The planners reason otherwise: the quota for building construction was issued only for a year, and it is necessary to use it in such a way as to designate on a chart a few more facilities. Then it may be reported that the uninstalled equipment is "attached" to the site. And how will it be for 1987? It's obvious. If the quotas prove insufficient, well then one has a legal basis to postpone the start of production.

New structures for 1986 were allotted less than 16 percent of the total cost of their construction, for the sole purpose of gaining a foothold at a site. Even for facilities begun long ago, the effort of operations has been carried beyond the limits of the planning year. Thus, they have been building the chemical production complex in Salavat for seven years, but the equivalent of half of the work has been carried over to the start of 1987. And this is not an exceptional case. Units begun prior to 1981 have been allotted less than a fifth of the means necessary for finishing operations. It is easy to see that the structures undertaken in the 10th Five-Year Plan, given such financing, will be completed after 1990.

As we see, the ministry confined itself to the designated allotment: a little money was given to all units. Can they cope at the building sites with these modest sums? Let us investigate the accounts. In the course of two subsequent five-year-plans the ministry obtained approximately a billion rubles per year for construction, but used a little over six hundred million. The capacities of the contractors serving the branch stabilized at this level. Now, having disregarded ten years of experience, the ministry has won for the next year an allotment of the sum of 875 million rubles. Will they be used? The items, drawn up in the ministry, are changed after the builders take them for use on actual jobs. And this is bad.

The ministry delegated the means, although modest, for constructing installations for primary oil refining in Kuybyshev and Syzran. Not long ago a brigade of specialists went to the location but didn't find a common language with the builders--they agreed to begin work on one installation only and set about allocating two million rubles per year instead of six, as in the item. This means that one facility has already "flown away" from the plan, and in another the operations will be perhaps what was really designated.

But if in 1986 there is no success in managing the allotment obtained, then operations worth 250-300 million rubles automatically transfer to the plan for

the next years. And as has already been said, the ministry has shifted the effort in construction plans to those remote years. Will it not happen, as before, that it will be convenient to carry over the periods for starting, that the branch will be even more strongly committed to an excessive number of projects, and that the huge capital expenditures will not give returns?

The leader of the Capital Construction Administration, A. Kuzmenko, answers no to this question. Although I will not say that anxiety does not gnaw at him. And he sometimes doubts the reality of that planned. And all the same he acts according to the departmental directive even though the projection for 1986 is inconvenient for the department itself: when the means are "padded", new facilities are not successfully done on time, and consequently, increases in production are also small. The delay in starting only two products--tires in Belya Tserkov and carbamide in Angarsk--turned out as a production shortage worth seven-eight billion rubles. I indicate for comparison: after four years the production output in the branch increased by 2.7 billion rubles. Similarly, the design of a plan for 1986 has been composed with a single goal: to show that the equipment reserves are being put into circulation.

But this is not the first five-year plan which does not obey the plans. In this case a "ritual" has been worked out for evading responsibility for the gap. I read orders, beginning from 1978. They differ only in their dates. They state in energetic expressions that necessary measures have not been taken, orders to take these measures are given and in conclusion--severe measures: such and such a person indicates that insufficient measures have been taken. The directive organs and control documents cite several other characteristics. Briefly, their thinking is as follows: the ministry planned very well, but the contractors are not carrying out the plans.

But why are they not coping well? Not only because they are overloaded by the unelevating tasks of the Ministry of the Petroleum Refining and Petrochemical Industry. Six years ago they delivered equipment for the second tire plant in Belya Tserkov. The unit is immense, but the efforts were great: two trusts were operating, especially created for the petroleum refining and chemical industry. They were to be allotted up to 40,000,000 rubles over a year's time. However, at the end of the first term this turned out not to be the case: the client allotted eight-nine million rubles per year instead. The builders began to search for more solid partners. Today the trust "Belotserkovkhimstroy" is working on approximately 30 units for 18 clients, and the trust "Promzhilstroy" on the whole has shifted its base to another town. Having lost through its own fault the capacities of contractors, the Ministry of the Petroleum Refining and Petrochemical Industry suddenly made a reassessment and planned rapid acceleration: from 11 million rubles allotted in 1984 to 57 million in 1986. Such jumps are by nature difficult to imagine, even if the contractor were to abandon all remaining clients. Naturally, builders do not accept the fantastic claim of the petroleum refining and chemical industry. The accumulated technology worth 135 million in gold still lies as it did. However, the unit is counted as started, the builders are held responsible for the derangement.

The story about this building is educational in another regard also. One of the leaders of the branch construction business confessed:

"Truthfully speaking, this unit is not terribly necessary. The facilities for tire production are redundant and it would be better to use the funds for reconstruction of operational factories. But it is necessary somehow or other to get rid of technological reserves...."

What does this mean--starts for the sake of starts? Just so, and not only in Belya Tserkov. Frequently, in production of new products there are no clients. For this reason in the past year the output of ethylene at four installations was reduced by hundreds of millions of rubles. It has come to the point that in Angarsk half of the ethylene produced was simply burned off in torches. It has been five years now since the petrochemists kicked up a row with the builders of Nizhnekamsk--this wrecked the start of a powerful production of reagents for the petroleum industry. Next year the unit will nevertheless start up, but First Deputy Minister N. Lemayev has noted that the oil industry workers have agreed to purchase only a small proportion of the reagents, and that no earlier than 1990.

This is again no exception to the rule. From a ruble of production funds introduced in the present five-year-plan, the branch takes away four times less product than from a ruble of old funds. A strange turn has been established. First of all they include in the plan the installation of technology purchased long ago (to immobilize the harsh criticism). And the new purchase? In the coming year the installation of barely one seventh of the new equipment will begin. In coming years the ministry will buy still more such technology. But when will there be time for it if the plan is above every measure overloaded with printed lines for new units in it and no chinks retained?

It would seem that something new is needed, from wheels to assembly. It is more than reasonable that new contracts are included under the urgent needs of the economy. For example eight installations will soon enter into production which should produce raw materials for the microbiological industry. In order to put them into operation, the less important or unreal units must be excluded from the construction plan. But then one must say honestly: it is necessary to reserve part of the construction, erect fewer units, the most necessary, with a view toward rapid entry into operation. The path is not the easiest, but there is no other.

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## METHODS TO INCREASE PETROLEUM PRODUCTIVITY DISCUSSED

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 15 Aug 85 p 2

[Article by Ye. Radchenko (director, Oil and Gas SRI, doctor of technical sciences) and G. Terentyev (laboratory chief for technical and economic research, candidate of economic sciences): "Depth Refining"]

[Text] If we consider that oil is a unique natural gift, which is a nonrenewable resource, the immense importance of using it rationally becomes obvious. Along with the economics of petroleum products in the area of consumption, the problem of improving petroleum refining processes and using of the raw material most effectively moves to the forefront.

The USSR energy program has provided for a reduction in the proportion of fuel oil in the total expenditure of energy resources for thermal power stations. This creates objective prerequisites for using extracted petroleum chiefly as raw material for producing motor fuel, liquefied gases, electrode coke and other valuable petroleum products. In other words, the agenda of the day has become the question of significantly deepening the petroleum refining process.

At the present time more than 40 percent of the total number of petroleum products produced consists of fuel oil, which is used as boiler and furnace fuel. Such use of a unique hydrocarbon resource is extremely irrational.

Modern processes such as catalytic cracking, hydrocracking and a number of other processes, meanwhile, make it possible to include fuel oil in refining processes and obtain from it additionally tens of millions of tons of valuable motor fuel and raw materials for petrochemicals. Calculations show that a broad introduction of technology in refining residual oil opens the possibility of increasing the depth refining of petroleum to 70-80 percent. The most important domestic effect of this is reducing the consumption of petroleum. A 1.2-1.4-fold increase in petroleum refinement compared to the current level would produce approximately an equivalent reduction in consumption of raw material.

Is the petroleum refining industry ready to solve this problem? With regard to scientific and technological matters, one may answer affirmatively to this question. In ours and other branch institutes, highly effective

depth refinement processes for petroleum have been developed. Mechanical engineers have also made their contribution: the production of basic instruments and equipment for a new generation of technological installations has been mastered.

Here one may not fail to note that thermocatalytic processes for depth refinement of petroleum residues occur at a high temperature, and in addition, several occur at high pressure in a hydrogen medium. This produces increased quality requirements for construction materials and instrument formulation and requires the use of costly catalyzers, which in the final analysis leads to increased capital, energy and maintenance expenditures in comparison with initial petroleum processing.

The combined and enlarged systems for depth refinement of fuel oil created by branch scientific research and design organizations make it possible to reduce these expenditures substantially. The first examples of such systems have been constructed during the current five-year plan at Moscow and Pavlodarsk oil refining plants. Their use has already made it possible to obtain an additional several million tons of light petroleum products without increasing the volume of petroleum refined.

Without a doubt removing fuel oil from the energy balance will make it necessary to substitute natural gas, coal or nuclear energy, which will require additional expenditures for the development of corresponding branches of the fuel-energy complex. Large one-time investments in creating facilities for depth refining in the petroleum processing industry will be necessary as well. However, in the final analysis, the economic effect according to estimates should comprise from 20-40 rubles per ton of fuel oil included in depth refining. In this case the expenditure for capital investment will be 2.5-5 times less in comparison with growth in volume of oil deposit.

Modern oil refining technology, the scientific and technological potential which we already have available, makes it possible, upon necessity, to achieve nonresidual petroleum refining, having increased to the maximum the production of fuel for internal combustion engines, aviation and ship engines, petrochemical raw materials and other valuable products. But the practical realizations of such refining processes are hindered due to a lag in native chemical and electrotechnical mechanical engineering and compressor construction. As a result, even newly created progressive processes are extremely high in metal and energy consumption. A serious obstacle on the path to a "non-residual oil" variant is also the insufficiency of highly effective catalyzers and the low level of use of secondary energy resources.

Large reserves for economical use of petroleum raw materials also exist at those enterprises where traditional refining processes are used. There is talk of intensifying and improving quantitative operating indices for installations and primary processing products for the purpose of increasing the selection of special purpose products.

The relationship here is direct: the increase of one percent in the selection of light petroleum products at primary oil processing installations is equivalent to a reduction in consumption of raw material by the same amount. In modern installations the separation of light petroleum products is close to their actual content in petroleum and reaches 95-96 percent of potential. At the same time, at plants of old construction, the proportion of which is rather high in the branch, the analogous index is 10-15 percent lower. If it is also taken into account that the aging equipment requires increased expenditure of energy resources, that here there are several times more maintenance and repair personnel required, the serious necessity to renew basic operating stock becomes obvious.

It should be realized that carrying out a program of deep petroleum refining, as well as the technological reequipping of branch enterprises on a modern basis will require significant capital investment and a specified amount of time. In the meantime, there is yet another way to obtain high results without such substantial expenditures, because of the more complete use of natural properties of petroleum.

The essence of the problem in brief is as follows. At the present time the quality of diesel fuel--the most massive type of combustible fuel for various transportation means and agricultural technology--is determined by a whole set of standards. They calculate its fractionating composition, viscosity temperature characteristics and certain other parameters. It would seem that this is fine--the standard would protect the quality. But if one looks from the point of view of using the petroleum raw material, you come to this conclusion: in a number of cases specified by the current standards the qualitative parameters aid an irrational consumption of petroleum.

Experiments and research conducted in recent years have shown that with a change in certain fuel quality parameters, it is possible to increase significantly the production volume of the fuel from the same quantity of petroleum, without resorting to the costly and energy consuming secondary processes. Optimization of the viscosity-temperature properties of diesel fuel, for example, make it possible to increase its separation from the raw material during primary distillation of petroleum by 3-3.5 percent. The basic technical maintenance characteristics of engine operation will remain without substantial changes.

The optimization of the "engine-fuel" system may give an additional several million tons of light petroleum products and economize hundreds of millions of rubles of capital investments in producing and refining petroleum. The first steps in this direction have already been taken: the Ministry of the Aviation Industry and the Ministry of the Maritime Fleet have been successfully persuaded in favor of changes in fuel standards. However, it is more difficult to find a common language with the ministries for the automobile industry, agricultural and tractor mechanical engineering and heavy machinery. Departmental interest, unfortunately, is still put ahead of considerations for economizing petroleum.

Since we are speaking of departmental preferences, one must not be silent about the following paradox: the USSR Ministry of the Petroleum Refining and Petrochemical Industry introduced deep refining processes for petroleum which were economically unsuitable. A number of branch indicators worsened because of it. Thus, there exists a clear contradiction between the branches and economic criteria of effectiveness.

Therefore, it is very timely that a restructuring of the economic mechanism occur in such a direction, as was noted in the June meeting of the CPSU Central Committee, to make the economy maximally receptive to scientific and technological progress, to ensure vital interests in this of all sections of the economy.

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MINISTRY OF CHEMICAL INDUSTRY FAILURE TO USE NEW TECHNOLOGY

Moscow SOTIALISTICHESKAYA INDUSTRIYA in Russian 30 Aug 85 p 2

[Article by Ye. Leontyeva: "Between 'Yes' and 'No'"]

[Text] Leaders of the Ministry of the Chemical Industry speak out for progressive technology for obtaining hydrogen peroxide. However, they are not taking practical steps for its realization.

In a review article on actions (16 April 1985) the newspaper informed the readers that the Ministry of the Chemical Industry continues to occupy a negative stance with regard to the progressive method. The official answer, signed by deputy minister Ye. Vlaskin, who has already retired, did not satisfy the editor. And this is understandable, since instead of concrete solutions we have received yet another, not the first by far, comparison of the anthraquinone method and its rival, the isopropyl method of obtaining hydrogen peroxide.

To what extent is a comparison possible? It is clear even to the nonspecialist that you won't get complete objectivity: the isopropyl method has been introduced in three factories; the anthraquinone method, after 17 years of conscientious service in industry, has been driven back to the GNIIKhTEOS laboratory. Chances are clearly not equal for them. Is it necessary to do this, even though world practice long ago carried out "natural selection", widely developing the method repudiated by us?

What is it that stands in its way? I have communicated with authors and planners, and I have ascertained that there is no hindrance now.

"We are ready to issue the total volume of original data for planning improved production," states V. Brudin, laboratory chief of GNIIKhTEOS.

"We may set about planning," states the institute planning director, O. Stuzhyk.

The action taken by the newspaper shook even the persistence of "rivals" from the Applied Chemistry State Institute in Leningrad--the cradle of the isopro-

pyl method. The chairman of the science council, B. Gidashev, expressing the collective opinion of this institute, now acknowledges that the technological possibility for developing industrial production of anthraquinone peroxide exists.

And so, has the ice melted? Has the stubborn "no" which has been heard for many years been changed at last to an open acknowledgement of the worths and improvements, having turned out to have been not a matter of technology? But the acknowledgement is still not a solution to the question, but only a step toward it. The branch staff is solving it. Repeatedly, I have turned there--this time to First Deputy Minister L. Osipenko. I explained that in answer to the action, they received an answer written for form only, but it was the actual facts, naturally, that interests us.

"I haven't read the article and have not heard of the action," the first deputy minister answered and requested a week to investigate.

And here is Osipenko's opinion a week later:

"Economics is for anthraquinone peroxide. We will build the first new plant for this method only."

Here it is--the long awaited "yes." How can we not rejoice--the ice has not only "broken up," but here is a real ice flow. I rushed to clarify when the first shop will be built, whether or not the funds have been allotted, where it will be and who will begin its construction?

"We cannot as yet begin construction," followed the sober reply.

I confess that before I went to L. Osipenko, I spoke with a number of branch staff specialists about the technological possibilities of creating a new plant. They undoubtedly exist. Earlier, Usolye was considered as a connection point--there at some time the construction of a peroxide plant which would use the technology which interests us had begun. Having swallowed up four million, the construction abated and no one has returned to it again. At the present, it is possible to pick more suitable sites, for example, Sterlitamak, where the association "Kaustik" produces unused hydrogen and oxygen as waste products, which are at the same time raw materials for hydrogen peroxide. This free raw material goes into the atmosphere at a rate of approximately 12,000 cubic meters per hour. This means from it one may obtain 24 tons of product per hour. Most of all, here is a powerful construction organization, although, incidentally, not occupied full-time.

Free raw material out of which one may get cheap peroxide is available also at one of the plants in Kazakhstan. Its leaders, on their own initiative, had already turned to GNIIKhTEOS, requesting an examination of the possibilities of producing peroxide at their plant. The plant workers had for a long time had ties with this institute, involving a whole series of research projects, so that their interest in the joint solution of problems is completely under-

standable. However, the ministry did not respond to their initiative. I asked Deputy Minister V. Romanov, handling the named enterprises, why it remained without attention.

"Not long ago, you asked me this same question," my interlocutor said in amazement. "I will give the same answer as then: don't we not have enough hydrogen peroxide in our country?"

Comrade Romanov was puzzled on the occasion when he was director of VPO, and is puzzled now, having become a deputy minister. Enviable consistency, I will say frankly. And it is characteristic that it does not depend on the post occupied.

But let us return to the first deputy minister. Unfortunately, the conversation on the possibilities, here also, in the final analysis, did not yield anything new, having stumbled on the irrefutable logic: "Why is it necessary to study this today? There are more urgent matters."

But what does the ministry prefer to study today? It turns out that it suggests broadening isopropyl production. As to anthraquinone productions, here, evidently, the thought is this: it has waited three decades and can continue to wait. As we see, rejoicing over the occasion of a firm "yes" has turned out to be premature. The more so since this is not "yes" but "maybe."

The indefiniteness of the situation and the streamlined answers of the leaders of the branch compelled the editor to turn to the party committee of the ministry so that he could finally make a major evaluation of the workers' position, responding to technological progress. As the secretary of the party Committee, R. Rumyantsev, reports, the criticisms have been acknowledged to be just. The Party committee did work with the leaders of the ministry and required the elimination of the practice of preparing answers to critical remarks of the press over the signature of persons not having direct relationship to the problems mentioned. He committed himself as well "to make an objective and major evaluation of the insufficiencies which the press has indicated in the operation of the branch, without permitting avoidance of real decisions."

But where is the long awaited answer to the question as to when the progressive method will be introduced into industrial production? Again there is no answer. Meanwhile, at a recent session of the board of the Ministry of the Chemical Industry and the presidium of the Central Committee of the branch trade organization, R. Rumyantsev devoted special attention to the statements of SOTSIALISTICHESKAYA INDUSTRIYA on the action "From Invention to Introduction," approved the principal position of the newspaper and even congratulated the editor because it showed the ministry this important problem which undoubtedly merits the most intent attention.

Is there anything new in the statement of the party committee secretary? No. It is still not clear what the outlook is for the introduction of the new technology during the 12th Five-Year Plan.

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## OIL, GAS INDUSTRY DEVELOPED IN FAR NORTH

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 1 Sep 85 p 2

[Article by G. Shmal, First Deputy Minister of Construction of Petroleum and Gas Industry Enterprises: "Let us Go Farther North"]

[Text] Among the many economic programs carried out by the Soviet people, the economic development of oil and gas deposits and the increase in production of oil and gas occupy a special role. In the resolutions of the 26th Party Congress, subsequent to the CPSU Central Committee Plenums, it was noted that the development of heavy industry is an unconditional prerequisite to solving all domestic problems--both production and social. Above all, this is true of its basic branches--fuel and energy.

In the last 20-25 years the average annual growth rate of capital investments in development of the fuel-energy complex has significantly exceeded the same indices for industry as a whole. This has made it possible to effectively involve the fuel-energy resources of eastern and northern regions of the country in the economic turnover--to create large regions of coal and gas production at accelerated rates in Western Siberia, Central Asia, Kazakhstan, Komi ASSR and the Southern Urals.

Special attention should be given to Western Siberia. At a session of the Politburo of the CPSU Central Committee which met at the beginning of August, the question of comprehensive development of the oil and gas industry of this region during 1986-1990, as well as ensuring fulfillment of quotas for the USSR Energy Program for production of oil, condensate and gas, were discussed. Among the notable measures were putting additional capacity into operation, increasing the volume of construction operations by a factor of 1.6 in comparison with the current five-year plan and creating broad program of transportation construction. In the 12th Five-Year Plan there will be a greater number of domiciles built, as well as items of significance to daily social and cultural life.

This places a special responsibility on builders building facilities for the oil and gas industry. Suffice it to say that they are faced with laying 155,000 kilometers of pipeline, a 1.7-fold increase over the present five-year

plan. Also, the number of installations for processing oil and gas, compressors, pumping stations and other units is growing significantly.

There is a good foundation for such an effort. Over the past years the branch has accumulated broad experience in effective operation, significantly increasing its material and scientific base. The results confirm this: the laborers of the branch will greet their professional holiday with overwhelming achievements. The five-year plan quota for volume of construction operations was met in March of the current year. The Western Siberian five-year plan had already been completed at the end of last year. The program to create the six-line system of gas pipelines from Western Siberia to central and western regions of the country was completed ahead of time.

Among the large-scale questions decided by the branch, a particular role is played by the comprehensive overstructure of the Urengoy gas-condensate deposit. In recent years, growth in the country's fuel deposits were ensured by the Urengoy industry. Since the beginning of the five-year plan, almost 900 million rubles of construction and installation work has been completed, and 10 installations for the comprehensive processing of gas, collectors, reservoirs and circuits have been constructed. Towards the end of this year the daily yield of deposits will reach projected level.

Such successes have resulted not only from technical reequipping of the construction organizations, improvement of the management structure, and restructuring of the economic mechanism. All this, of course has had a great economic effect. But the main moving force behind our achievements has been the people--their accelerated work and creative search for reserves. The initiative of progressive collectives which assumed the obligation to fulfill the five-year plan quotas for basic technical and economic indicators by August 1985 has received the broad support of the enterprises of the Ministry of Construction of Petroleum and Gas Industry Enterprises.

The initiators of the preanniversary competition reached the designated goals ahead of schedule. This includes the comprehensive production line collective of the trust "Tatnefteprovodstroy," headed by Hero of Socialist Labor, Ilyur Shaykhutdinov. In the first half year, the production line completed its quota for oil pipeline construction in Srednoye Priobye, relocated at the Yamburg-Yelts-1 pipeline construction site, and now leads in the competition on this route.

A brigade of the association "Sibkomplektmontazh," led by Lenin Prize laureate Anatoliy Shevkoplyas, has also successfully met its obligations. The brigade of Vyacheslav Lukyanov was distinguished in the competition, having completed 6.4 million rubles worth of construction in excess of the five-year plan. This collective is known as the winner of the All Union Socialist Competition in Honor of the 50th Anniversary of the Stakhanovite Movement, and brigade leader Lukyanov is worthy of the K. S. Brekhov Soviet Trade Union Prize for 1985. The obligation was met to complete insulation packing tower SMU-16 ahead of the scheduled completion time for the five-year plan by the

"Ukrtruboprovodstroy" trust, where brigade leader is Nikolay Shevchuk. Because of the tower there are more than 450 kilometers of pipeline.

The laborers of the branch have a right to be proud of their successes. However, ahead lie still more difficult problems and stressful and responsible work. In all collectives increased socialist obligations in honor of the impending 26th Congress of the CPSU have been adopted and carried out, and the Volga automobile workers' initiative has received approval. The upcoming plans for the 12th Five-Year Plan have been developed. Carrying them out requires a more energetic search for ways of increasing effectiveness of industrial construction, a reduction in the period required for installation of lines and platform units, and unification of efforts by construction workers, metallurgists, chemists, industrial engineers and scientists in solving problems which arise.

In the 12th Five-Year Plan for the branch, the complexity coefficient for operations has increased sharply. In oil regions this results from going out to new deposits located a significant distance from the base and communications. They are starting practically from zero at the Tengizskoye and Zhana-zholskoye deposits. For the gas industry, Karachaganak and Yamburg present the greatest difficulty. It is hard to imagine more difficult and complicated conditions than in these regions. In Karachaganak there is no water, and the surface of Yamburg consists of masses which are 70 percent ice. In one area in the summer the heat is up to plus 50 degrees; in the other the winter frost is minus 55 degrees.

At a meeting of the ministry's most active members concerned with scientific and technical development of the branch in 1986-1990, ways of sharply increasing the operational effectiveness were noted. One of these is the broadening of scales for using the comprehensive block method, increasing the degree of plant preparedness, changing where possible to a superunit, the use of which will be very effective. Facilities at the Yamburg deposits have already been designed in a superunit variation, which will make it possible to shorten the construction period by several times. Measures for automating welding operations have also been noted and established. This will sharply increase their quality and decrease the dependency on weather conditions.

Another direction for increasing the effectiveness of construction productivity is the further development of the engineering itself, broadening nomenclature and increasing the quality and reliability of machines and mechanisms which are produced.

In the branch today rotor excavators, pipes, pipe-laying cranes and other mechanisms are being produced. However, this is still not enough. And in this regard, we must criticize the engineers. They are not sufficiently active in reequipping our branch. The pipe-laying crane problem seems particularly severe to us. A paradox has developed: we produce more tractors than any other place in the world, but we turn to the foreign market for pipelayers and bulldozers.

This problem becomes especially severe with regard to active production in the region of the Far North. The severe climate dictates its own conditions here. And the time has come to examine all the unsolved problems in the complex and create a different technique, taking into account the ecological aspects governing this region. Here science has the first word.

Ahead are new, more complicated goals. They have been indicated in the resolution of the CPSU Central Committee and the USSR Council of Ministers, "On Further Developments of Industrialization and Increase of Labor Productivity in Capital Construction." And laborers of the branch will exert every effort to solve the main problems--hurrying to make units operational more quickly, using every kind of economy and thrift and increasing the quality and effectiveness of all our work.

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OIL, GAS WORKERS HONORED

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 1 Sep 85 p 2

[TASS article, "In Honor of the Celebration"]

[Text] Large fuel pipelines are being laid successfully during the 11th five-year plan. All gas pipelines from Urengoy have been constructed ahead of the specified date. This has made it possible, additionally, to supply consumers many billions of cubic meters of valuable raw material and also to set about laying the Yamburg-Yelets-1 main line, of which more than 2,000 kilometers have already been laid, which exceeds the plan. The gas workers work constantly to increase the work pace, having extracted since the beginning of the five-year plan considerably more valuable raw material than the plan called for. The oilmen are prospecting for ponderable operating reserves. This was discussed at the celebration meeting, honoring Oil and Gas Industry Workers Day. It took place 30 August in Moscow.

In the presidium were Secretary of the CPSU Central Committee, B. N. Yeltsin; Deputy Chairmen of the USSR Council of Ministers, N. K. Baybakov and B. Ye. Shcherbina; CPSU Central Committee Department Chief, I. P. Yastrebov, and leaders of a number of ministries and departments.

V. G. Chirskov, Minister of Construction of Oil and Gas Industry Enterprises, gave a report.

The participants of the celebration meeting affirmed that the petroleum, gas and construction workers on the fuel supply lines, having shown socialist competition in honor of the upcoming 26th Party Congress, are applying all effort, knowledge and experience in order to successfully complete the five-year plan tasks and are making a weighty contribution toward strengthening the fuel-energy potential of the country.

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## WESTERN SIBERIAN OIL AND GAS INDUSTRY

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 4 Sep 85 p 2

[Unsigned article: "Resources of Tyumen Geologists"]

[Text] Recently, the Politburo of the CPSU Central Committee discussed the problem of the comprehensive development of Western Siberia's oil and gas industry. At the request of the editor, F. Salmanov--Hero of Socialist Labor, Lenin Prize laureate and director of the Main Administration for Tyumen Geology--discusses the work of geologists in this leading fuel producing region of the country.

From year to year the technological equipment of geological prospectors increases. One need only mention the display equipment alone, with which the services of the main administration and associations are equipped. Now, in a matter of minutes we receive daily reports on drilling, tower construction and other operations. Press the key, and onto the screens comes information on literally thousands of boreholes. At one time we only dreamed of such a thing. Naturally, the effective management of subdivisions has increased significantly.

Many technological innovations are located directly at sites. These include vibrators, which geophysicists use to obtain complete information on the earth's crust without labor intensive explosives operations, and the new turbodrills, which increase the rate of penetration by one and a half times. In a word, our technological capacities have become much greater, but indeed, the demand has also increased and the volume grown.

The Western Siberian oil and gas complex will play a decisive role for many years to come in the development of fuel and energy branches. The continuous growth in oil and gas production requires guaranteed reliable stores of raw materials. Therefore, it is necessary to increase the volume of geological prospecting operations. During this five-year plan we will drill 6.9 million meters of boreholes, which is twice as much as we drilled previously.

In order to maintain the rate of increase in oil and gas, to ensure a continuous growth in level of extraction, in the next five years it will be necessary to drill 14 million meters of search and exploration boreholes. Given the existing organization of geophysical and borehole operations and production management, given the techniques, technologies and management structure available, this will be practically impossible to do. Hence, no less than 130 new drill brigades have to be created. The total number of all workers in the main Tyumen Geology needs to be doubled. So, to resolve the problem, as we see, isn't very simple.

It is of primary importance to use available resources. And they are plentiful in seismic prospecting, tower construction, drilling and borehole testing. All our 62 parties now use the new methods of recording and processing materials. Computer processing centers have begun to operate. Thus, labor productivity among geophysicists has grown immeasurably. However, during the next five-year plan the volume of their work will increase three to four times. It will be necessary to create a network of computer centers for all geophysical expeditions and equip them with the latest computers. Unfortunately, industry has as yet been somewhat slow in meeting our needs.

Further increase in geological prospecting productivity requires radical reequipping based on modern science and technology. First of all, it is necessary to accelerate the installation of drilling equipment. Here much, but by no means all, depends on the drilling brigades. New installations are necessary which could be mounted more quickly and easily, which would be more transportable and have better use qualities. Now, exploration halts at great depths. We await new equipment which would allow exploration to be done for oil and gas at depths of 4,000-6,000 meters.

We see great resources in the improvement of specialized transport for geological prospecting operations. Because of the lack of roads, after finishing operations a part of the machinery remains idle. There is no way to transport it to a new location. Talk about transport by air cushion has drug on, which we expect will remain talk for the present.

Yet another direction in using available potential is the improvement of techniques and technologies of the drilling process itself. Improvement in brigade work is a most important indicator.

Of course, skill is not a concern for the Tyumens. An illustration of this is the achievement of the drilling brigades lead by Aksarin, Ishanbayev, Kamyshin, Solov'yev and other of our foremen.

But for the successful solution of the problems skill alone is not enough. A creative approach and constant searching are necessary. Such an example is found in the borehole experimentation brigade of the Tazovskiy arctic expedition, where the foreman is a laureate of the USSR State Prize, A. Myltsev. This collective first introduced sand-blast drilling, the propellant pressure generator and a number of other innovations. Therefore, their results are greater than in other places. We have modelled the studies of the All Union School of Advanced Experimentation on the basis of this brigade.

An innovative approach to the matter is required today particularly from leaders of all ranks. We do have such people. The collective of the association "Obneftegazgeologiya" had for several years in succession been stagnant. When they elected V. Parkhomovich, a certified engineer and good production organizer, the association began to come up. It doubled the volume of search operations. The collective is the first in the branch to report the completion of the five-year task for growth of oil and gas reserves, and has become the recognized leader of the precongress labor watch.

The multithousand-member collective of the Main Administration for Tyumen Geology, according to results of the first half year of operation, has become a winner in the All Union Socialist Competition and is worthy of the challenge Red Banner of the USSR Ministry of Geology and the Central Committee of the branch trade union. We regard this year's successes as a basis for accomplishing the comprehensive and important tasks of the 12th five-year plan.

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## GORBACHEV AT WESTERN SIBERIAN GAS FIELD

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 6 Sep 85 p 1

[TASS article: "M. S. Gorbachev's Visit to Urengoy and Surgut"]

[Text] General Secretary of the CPSU Central Committee, M. S. Gorbachev, arrived at Urengoy, a major gas producing region, from Nizhnevartov on 5 September. Ten main pipelines, supplying the country's economy with natural gas, originate from here. During the first year of the upcoming five-year plan, production from this deposit will increase to the projected level for natural gas output. Simultaneously, gas condensate production will also increase.

M. S. Gorbachev visited a powerful installation for comprehensive preparation of gas--one of the foremost facilities of the branch. He examined the progressive technological equipment for domestic production, used by the collective of the installation to reach the highest productivity in Western Siberia--20 billion cubic meters of gas per year. Progress on the work of creating an automatic control system for technological processes based on microprocessors was reported, the installation of which is being completed. This will ensure the operation of the facility with practically no maintenance personnel, the greatest qualitative preparation of raw material and its rational use. Systems similar to this have already been installed at a number of facilities. They are envisaged for use in the complex weather conditions of the Far North, particularly at the Yamburg gas deposits.

M.S. Gorbachev stressed that the broad application of automation, electronics and microprocessor technology will ensure a resultant higher gas output with a significant reduction in labor expenditure. Acceleration in the pace of scientific and technological progress is the main trend for stable development of the fuel, energy and raw materials base of the economy. During conversations with workers and specialists he was interested in details of how planning tasks and socialist commitments are being fulfilled. Gas workers and construction workers discussed the competition of their collectives in honor of the impending 27th CPSU Congress. In honor of the opening of the Congress increased commitments for above-the-plan gas production were adopted.

M. S. Gorbachev visited a plant for comprehensive preparation of gas condensate for transportation. Creation of such enterprises opens the way for more effective use of natural riches of the deposit.

During the second half of the day M. S. Gorbachev visited Surgut.

He examined the Surgut GRES, which is called here the energy heart of both the oil industry and the towns of Srednyiy Priob. The capacity of the operational phase is 3,300,000 kilowatts and capacity under construction is 4,800,000 kilowatts.

M. S. Gorbachev acquainted himself with the progress in constructing GRES 2. Construction began on its first power unit, with a capacity of 800,000 kilowatts, in the spring of this year. He talked with installers and testers, who are preparing the second unit for start-up at the end of the month. The GRES operates on petroleum by-product and natural gas, thanks to which the cost of electric power is significantly reduced. It was stressed that the use of domestic science and technology during the construction of the Surgut GRES increased the reliability of the power supply to the oil and gas industry facilities of Western Siberia.

Then, M. S. Gorbachev visited the central base for production maintenance of electric drive installations, where petroleum and gas technology was examined. Equipment for carrying out underground and capital repair of boreholes, aggregates for mechanized operations, technological transport and cross-country machines were demonstrated. During the inspection particular attention was given to the necessity for increasing the quality of items.

M. S. Gorbachev noted that the main lever for intensifying the economy, the best use of accumulated potential, is the cardinal acceleration of scientific and technological progress. With the perfection of current technologies and the modernization of machines and equipment should come the transition to principally new technological systems, to high quality technology of the most recent generations, which will give the highest effectiveness.

In the Surgut gorkom a discussion occurred between M. S. Gorbachev and leaders of ministries, associations, local party, soviet and economic organs, and specialists. Acceleration of development in Tyumen Oblast of the petroleum industry, electric power, transport construction, comprehensive erection of residences and social and cultural facilities were discussed.

In the conversations, which were sincere and businesslike in nature, the workers of the enterprises, the inhabitants of New Urengoy and Surgut, told Mikhail Sergeevich that they and their labor collectives wholeheartedly approved and supported the course of the party toward strengthening discipline and order, the eradication of drunkenness, the line taken in the battle for economy and thrift of each person at his work station.

Accompanying M. S. Gorbachev on the train to Urengoy and Surgut were Candidate Member of the Politburo of the CPSU Central Committee and Secretary of the CPSU V. I. Dolgikh, CPSU Central Committee Secretary B. N. Yeltskin, Deputy Chairmen of the USSR Council of Ministers A. K. Antonov, N. K. Baybakov, B. Ye. Shcherbina, and first Secretary of the Tyumen party obkom, G. P. Bogomyakov.

On 5 September, M. S. Gorbachev left Surgut for Tymen.

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## BRIEFS

**MOLDAVIAN IMMERSION PUMPS SENT TO SIBERIA--Kishinev--**The last batch of this year's targets of immersion pumps was sent to the oil workers of Tyumen by the workers of Moldavgidromash Association. Fulfilling these orders was a task of special importance in the collective, one of the basic directions of socialist competition of shops, sections, and brigades. For more than 10 years pumps with a Moldavian trademark have been reliably serving oil extractors in Surgut, Samotlor, and other oil deposits of West Siberia. And the contract obligations are always fulfilled on time. [By A. Pasechnik] [Text] [Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 3 Oct 85 p 2] 12255

**OIL PLAN OVERFULFILLED--Udmurt ASSR--**Miners of Udmurt ASSR have begun working the new Kyrykmasskoye oil field. It is located in the region of Serapul, where a leading collective of oil extractors is at work, producing more than 5,000 tons of fuel above the plan since the beginning of the year. Making wise use of the existing supply of wells, they have done everything to accelerate the startup of another oil field, and fulfill in a timely fashion their socialist obligations in honor of the 27th Party Congress. Shaft sinkers are also working in a well-coordinated fashion, drilling more than 10,000 meters of rock in addition to the plan. The highest indicators belong to the brigades of V. Bykov and Yu. Gausknekht, which dealt in a timely fashion with targets both of this year and the 5-year period as a whole. This made it possible for the Udmurtneft Association to exceed the schedule of extraction by 25,000 tons. [By V. Ukolov] [Text] [Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 18 Oct 85 p 1] 12255

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## PIPELINE SHOCKWAVE PROBLEM SOLVED

TASS in Russian 0930 GMT 25 Oct 85

[Summary] Scientists at the Institute of Chemical Physics of the USSR Academy of Sciences have learned to fight the dangerous shock wave which can arise in the transportation of oil and gas.

Two-phase systems, consisting of liquid and gas, are becoming ever more common in modern technology. The use of air/water and oil/gas mixtures in steam generators, in heat exchangers in atomic reactors, and in cryogenic technology, and especially the transportation of such mixtures, have sometimes caused great difficulties. Under certain circumstances a kind of shock wave can arise in gas-liquid mixtures, which is capable of destroying an oil pipeline or reservoir, causing explosions and fires.

From now on, not a single oil and gas pipeline will be built without the recommendations of specialists from the Institute. This is extremely important for Soviet pipelines, which are now almost six times as long as the length of the Earth's equator.

/12955  
CSO: 1841/87

UDC 620.197.323:665.6

TREATMENT OF CORROSIVE RECIRCULATING WATERS AT PETROLEUM REFINERIES

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 9, 1985 pp 11-14

SOROCHENKO, V. F., SUPRUNCHUK, V. I. and KOZLIKOVSKIY, Ya. B., Kiev Polytechnic Institute

[Abstract] A minireview is provided of the problems of corrosive recirculating waters at refineries and the methods of their treatment, based on a survey of recent Soviet literature. There is general agreement that the most effective approach to this problem consists of a complex of chemical treatment procedures, including purification, stabilization, and anticorrosive reagents. Such treatments prolong the service life of equipment and installations, and make possible the use of low-alloy steel at refineries. Examples are cited of the use of various corrosion inhibitors, including IKB-4. Complete biochemical purification is achieved when the IKB-4 absorbent is used in a concentration of 25 mg/liter, but the effectiveness of IKB-4 is highly dependent on the method of its preparation for use. In general, nontoxic passivating inhibitors function best in recirculating systems with mixed oxygenhydrogen depolarization. Among these inhibitors some of the most promising have been identified as phosphorus compounds, especially polyphosphates and their formulations with inorganic and organic additives when used in concentrations of 15-20 mg/liter. Figures 2; references 25 (Russian).

[111-12172/12955]

UDC 661.183.6+665.656+542.97:547.12

HIGH-SILICON ZEOLITES IN OIL REFINING

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 9, 1985 pp 18-21

NEFEDOV, B. K., All-Union Scientific Research Institute of the Oil Industry

[Abstract] A summary is presented of some recent advances in the use of high-Si zeolites in catalytic refining, with particular attention given to two novel Soviet products, TsVK and TsVM. The former has a  $\text{SiO}_2:\text{Al}_2\text{O}_3$  molar ratio of 70-100 and is synthesized in the presence of organic matter, while TsVM has a  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio of 35-50 and is produced in the absence of organic matter. To date, these two types of zeolites have been utilized successfully in selective deparaffinization of petrochemical products and as catalysts in xylene isomerization, preparation of synthetic fuels, and in isomerization of pseudocumene. The other uses to which the catalytic properties of TsVK and TsVM have been applied include hydroisomerization of the hydrocarbons of gasoline fractions and disproportionation of aromatic hydrocarbons. Figures 1; references 11 (Russian).

[111-12172/12955]

UDC 66.097;665.644.4:547.21.07

CONTROL OF AROMATIC HYDROCARBON PRODUCTION ON L-35-6 INSTALLATION

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 9, 1985 pp 22-24

SHPUNT, M. I., MELMAN, A. Z., DANILOV, N. A., LOZINSKIY, V. N. and OVCHINNIKOVA, T. F., Novo-Yaroslavl Refinery; IPKneftekhim (expansion unknown)

[Abstract] Technical details are presented on the operation of an L-35-6 installation at catalytic refineries for the production of aromatic hydrocarbons, with a view toward defining and improving process control parameters. Statistical data are tabulated on the various parameters of the technical process and on the quality of the raw materials and catalysts. The data were then analyzed and applied to design of efficient operating conditions for the synthesis of benzene and toluene at L-35-6 using selected algorithms. The algorithms provided for the proper ration of benzene- and toluene- yielding hydrocarbon starting materials, selection of raw material quality in relation to availability and economic factors, and for constant monitoring of the hydrocarbon feed to meet changing demands for toluene and benzene. Figures 1; references 12: 11 Russian, 1 Western.  
[111-12172/12955]

UDC 665.765-404:621.771

TESTING OF LUBRICANT VNII NP-261

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 9, 1985 pp 29-30

SHADKINA, S. L., PUNKTOVA, O. N. and CHERTKOVA, N. Ya., State Scientific Research Institute of Arctic Geology

[Abstract] Trials were conducted with a novel lubricant, VNII NP-261, designated to replace NK-50 for use in airplane and helicopter roller bearings. The service lifetime of NP-261 has been shown to exceed, 1.5- to 2-fold, that of NK-50, on the basis of 500-1050 useful summer hours of service. With further improvements, the useful temperature range of NP-261 now covers a span from -55 to +45°C when used on civil aviation aircraft.  
[111-12172/12955]

SPECTROSCOPIC STUDY OF PETROLEUM OF KUMKOL DEPOSIT

Alma-Ata VESTNIK AKADEMII NAUK KAZAKHSKOY SSR in Russian No 8, Aug 85 pp 70-72

TEREKHOVICH, S. L., ZAMYATINA, G. M., ALPAYEV, A. A., MUSALIMOV, S.

[Abstract] The Kumkol oil field in Southern Kazakhstan was discovered as a result of geological explorations in the southern Turgaysk basin. Results are given of a study of oil samples from the Kumkol field by IR spectroscopy and atomic absorption to establish the characteristics of its hydrocarbon composition and the concentration of some metals. Two samples of raw unfractionated petroleum from the Kumkol field from the Neomacian deposits of the Lower Carboniferous period (well 1, 1067-1115 m drilling interval) and from the Jurassic horizon (well 3, 1321-1328 m drilling interval) were studied. The petroleum from this deposit is light with a density of 0.82-0.83 g/cm<sup>3</sup>, with low sulfur of 0.33-0.55% and a high paraffin content of 11%. The spectrographic characteristics for the oil from wells 1 and 3, respectively, are: ratio of aromatic hydrocarbons to normal paraffins 0.21, 0.31; aromatic to paraffin hydrocarbons 0.06, 0.05; naphthenes to paraffin hydrocarbons 0.05, 0.05; normal paraffins to paraffins 0.22, 0.15; and substituted paraffins to paraffines 0.52, 0.43. The absence of the carbonyl group indicated that the oil was not oxidized. The data indicate that the samples from both wells are similar. These samples were compared to data from petroleum samples from the Triassic and Jurassic producing layers of the Uzen deposits, Southern Zhetybay and from the Carboniferous deposits of Kenkiyak and Tortay are found to be similar. The content of vanadium and nickel is 0.0005% and 0.0003%, respectively, which is significantly below the clarke for sedimentary rocks. Iron is present in small amounts (0.0028 and 0.00047%). The low concentration of metals conforms to the characteristics of the hydrocarbon composition of the oil, which is a predominance of the paraffin structure with low content of naphthenes-aromatics. A high concentration of V and Ni is typical for heavy high sulfur petroleums rich in asphalt-resin components. Obtaining information on the characteristics of the oil from the Kumkol field by spectral methods can be valuable for examining the geological questions of genesis and conditions for petroleum accumulation. Combining two relatively simple analytical methods is very effective for initial diagnosis of raw petroleum and should precede any detailed study of its individual fractions. Figure 1; 3 Russian references.

[30-12886/12955]

SEPARATION AND CHARACTERISTICS OF COMPOSITION AND PROPERTIES OF HYDROCARBONS AND TARS ASSOCIATED WITH ASPHALTS

Ashkhabad IZVESTIYA AKADEMII NAUK TURKMENSKOY SSR: SERIYA FIZIKO-TEKHNICHESKIKH, KHIMICHESKIKH I GEOLOGICHESKIKH NAUK in Russian No 3, 1985 pp 40-44

TAIMOVA, B. A., TALALAYEV, Ye. I., SERGIYENKO, S. R., NURMUKHAMEDOVA, O. T. and GALPERIN, I. M.

[Abstract] The composition and properties of hydrocarbons and tars coprecipitating with asphalts was compared with those extracted directly from the residues over 723°K of petroleums from the Oval-Toval and Koturdepe fields. The samples were extracted with normal hexane and subjected to eluent adsorption chromatography with a series of organic solvents. The chemical nature of the petroleums is clearly expressed in the component grouping compositions of the asphalt-associated compounds. These differ from the initial petroleum residues -- particularly noticeable was a sharp rise in the amount of bicyclic compounds and a lowering of the polycyclic compounds. The tars also differ in their solubility in isoctane, with the ones from residues having a significantly smaller insoluble fraction. Ultraviolet spectra of the fractions indicated the presence of substituted benzene rings as well as the presence of nitrogen, oxygen and sulfur. Curves of mass-molecular distribution showed that the samples from the residues had no more than 5-15% of compounds in the higher molecular weight zone, while those with the asphalts had about 25%. Figures 4; references 3 (Russian).

[52-12672/12955]

VERY SIMPLE METHOD OF COOLING GAS

Ashkhabad IZVESTIYA AKADEMII NAUK TURKMENSKOY SSR: SERIYA FIZIKO-TEKHNICHESKIKH, KHIMICHESKIKH I GEOLOGICHESKIKH NAUK in Russian No 3, 1985 (manuscript received 5 Nov 82) pp 98-99

MAMEDOV, M. and BERDIYEVA, Dzh. K., Scientific Production Association "Solntse," TuSSR Academy of Sciences

[Abstract] Natural gas can be cooled in an arrangement of water-filled trays with a central gas-carrying tube. Heat-balance equations for this scheme are provided. They assume that there is thermodynamic equilibrium within the system and that gas and water temperatures are solely a function of tray length. Verification of the equations on an experimental apparatus gave satisfactory agreement for the gas temperatures, but the water temperatures differed from the calculated values -- apparently because the equation assumed convection only within a cross-section and not parallel to the long axis. Figures 1; references 3 (Russian).

[52-12672/12955]

PHARMACOLOGY AND TOXICOLOGY

UDC 615.015.1

PREDICTION OF TOXICITY OF SOME 8-AZASTEROIDS

Minsk VESTNIK AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIKH NAUK in Russian No 4. 1985 (manuscript received 15 Nov 84) pp 115-116

SOKOLOV, Yu. A., GOLUBOVICH, V. P. and AKHREM, A. A., Institute of Bioorganic Chemistry, BSSR Academy of Sciences

[Abstract] A prior study of 32 azasteroids indicated that the electron densities at carbons 2 and 3 were the most indicative quatochemical parameters of toxicity. This article presents calculated electron densities at these carbons for an additional 35 nonsynthesized azasteroids, differing in groups attached at positions 2, 3, 15 and 15' (16 and 16' for compounds with a six-membered final ring) and in -O- or -NH- at position 16 (17 for six-membered rings). Based on these electron densities and the earlier correlation equations, multiple linear regression is used to compute a predicted toxicity (LD<sub>50</sub>) for these compounds. Tabulated data shows significant toxicity is predicted for only eight of the compounds. References 4: 1 Russian, 3 Western.

[29-12672/12955]

UDC 547.853.3'735.04:543.422.4

CONVERSION OF 5-METHYL-6-CARBETHOXY-3,4-DIHYDROTHIENO[2,3-d]-PYRIMIDINE TO OBTAIN 4-METHOXY-, 4-ALKYLAMINO- AND OTHER DERIVATIVES OF THIENO[2,3-d] PYRIMIDINE

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian Vol 217, No 6, Jul 85 (manuscript received 23 May 84; in final form 11 Sep 84) pp 925-928

GRINEV, A. N. (deceased) and KAPLINA, N. V., All-Union Scientific Research Chemical Pharmaceutical Institute imeni S. Ordzhonikidze, Moscow

[Abstract] Various derivatives of thienopyrimidines are known to have anti-viral, antibacterial and antiparasitic action, but certain variants have received little scientific interest. The present article reports on

conversions of 5-methyl-6-ethoxycarbonyl-3,4-dihydrothieno[2,3-d]pyrimid-4-one. Special interest has been directed at 4-chloro-substituted thieno[2,3-d]pyrimidines as intermediate compounds in the synthesis of other aminoderivatives that are regarded as antimetabolites of natural purine bases. The electron-acceptor substituent in position 6 was found to increase the receptivity of chlorine to nucleophile substitution. In this manner the authors obtained 4-methoxy-, 4-alkylamino- and 4-dialkylaminoderivatives of the initial compounds. Results of alkaline hydrolysis and bromine treatment are also outlined. Processing of 5-dimethylaminomethyl-4-methoxy-6-ethoxycarbonylthieno[2,3-d]pyrimidine with nitrogen chloride at room temperature led to demethylation in position 4 and formation of a corresponding hydrochloride. Data on synthesis procedures are provided. References 5: 1 Russian, 4 Western.

[40-12131/12955]

UDC 547.854.7'859'867.8:543.422

#### SYNTHESIS OF CERTAIN PYRIMIDO[4,5-b]OXAZINES BASED ON 5-AMINOPYRIMIDINES

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian Vol 217, No 7, Jul 85 (manuscript received 10 Jul 84 in final form 10 Nov 84) pp 974-976

MELIK-OGANDZHANYAN, R. G., KHACHATURYAN, T. A., MIRZOYAN, V. S., MANUKYAN, A. G. and STEPANYAN, G. M., Institute of Precision Organic Chemistry, ArSSR Academy of Sciences, Yerevan

[Abstract] Although it has received little study, the system of pyrimido[4,5-d]-[1,4]oxazine is promising as a potential cancerolytic since it is an oxygen analogue of pteridine, the basis of folic acid. The present article reports on study of previously obtained 5-aminopyrimidines with chloracetic acid, producing 2-methyl-4-chloropyrimido[4,5-b][1,4]oxazinone-6. The latter's structure was confirmed by an analogous cyclization. Toxicity and antitumor activity on sarcoma-45, the Walker carcinosarcoma and the Ehrlich ascitic carcinoma were studied, showing that the absolute lethal doses of the compounds synthesized for white mice were 1.25-1.5 gram/kg. The substances did not, however, have impressive antiblastic activity in relation to the indicated tumors. Data on synthesis of the tested compounds are presented.

References 7: 3 Russian, 4 Western.

[40-12131/12955]

2,5-DISUBSTITUTED FURANS IN SYNTHESIS OF 2-CYCLOPENTENONE DERIVATIVES

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHMICHESKAYA in Russian No 4, 1985 (manuscript received 22 Feb 85) pp 465-472

LOZHA, E. V., LOLYA, D. O., FREYMANIS, Ya. F., TUROVSKIY, I. V., GAVARS, M. P. and LIYEPINYA, A. Ya., Institute of Organic Synthesis, LaSSR Academy of Sciences

[Abstract] A five-stage method has been devised for the synthesis of dialkylacetals of 3-formyl-4-oxy-2-methoxycarbonylmethyl-2,5-dihydrofurans, starting with 5-formyl-2-(2'-methoxycarbonylethyl)-furan (I), as a starting point for the eventual synthesis of prostaglandins. The synthesis of II was achieved via the Wilsmeyer reaction, involving formylation of methyl 3-(furyl-2)-propionate. The key step in the synthesis is represented by the selective splitting of the dihydrofuran ring of the dialkylacetals of 5-formyl-2-(2'-methoxycarbonylethyl)-2,5-dimethoxy-2,5-dihydrofuran. Cyclization of the resultant 1,4-diketones into the dialkylacetals of 3-formyl-3-oxy-2-methoxycarbonyl-methyl-4-cyclopenten-1-one represents the final step.

References 10: 2 Russian, 8 Western.

[71-12172/12955]

POLYMERS AND POLYMERIZATION

BRIEFS

ALL-UNION CONFERENCE ON HIGH-MOLECULAR COMPOUNDS HELD--(TASS, Alma-Ata)--In the capital of Kazakhstan, the 22nd All-Union Conference on High-Molecular Compounds completed its work. "Surpassing traditional materials such as metal, wood and leather in their strength, light weight, and thermal stability, polymers are becoming truly universal replacements for them," observed Academician V. Korshak, chairman of the USSR Academy of Sciences Scientific Council on High-Molecular Compounds. "Rubber, vulcanized rubber, plastics, film and lacquer coverings, and synthetic fibers have found a worthy place in various sectors of the economy and settled firmly into the existence of Soviet people." Thanks to the discovery of specific properties of high-molecular compounds, it has become possible to create materials which have no analogues in nature, allowing us to resolve qualitatively new tasks. The conference discussed, in particular, questions of creating incombustible light-sensitive polymers which would make it possible to avoid using silver in photography. Materials have already been obtained which can conduct an electrical current well, but we still face the task of obtaining superconducting polymers. Participants in the conference focused special attention on problems of adopting the achievements of science in practice. [Text] [Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 20 Oct 85 p 2] 12255

CSO: 1841/67

MICROSUSPENSION POLYMERIZATION OF METHYLMETHACRYLATE AND STYRENE

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 284, No 4, 1985  
(manuscript received 18 Sep 84) pp 908-911

SEMCHIKOV, Yu. D., SLAVNITSKAYA, N. N. and MYAKOVA, N. A., Scientific Research Institute of Chemistry at the Gorkiy State University imeni N. I. Lobachevskiy

[Abstract] A one-stage method of producing microsuspension polymers with particle sizes of 1-10  $\mu\text{m}$  was developed. Intensive mixing (2000 rpm for 15-30 s) of the monomer suspensions in the presence of an emulsifier (E-30, "volgonat") and a high-molecular-weight dispersion stabilizer (a hydrolyzed copolymer of styrene and maleic anhydride) was insufficient to provide the desired particle size. The choice of a surface-active initiator also had a significant effect on the stability of the suspension, with lauroyl peroxide providing the best results by forming a protective adsorbent layer at the droplet-liquid interface in conjunction with the emulsifier. This changed the reaction kinetics, increasing the initial reaction speed several fold by lowering the  $E_a$  of the reaction to 52 kJ/mole. Apparently polymerization takes place mainly at the droplet surface, forming a "skin" which acts as a supplementary barrier against the coalescence of individual droplets. This provided suspensions with particle sizes of 1-6  $\mu\text{m}$ . Figures 2; references 5: 2 Russian, 3 Western.

[55-12672/12955]

POLYMERIZATION OF ETHYLENE ON SURFACE OF DIAMOND AND GRAPHITE

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 284, No 4, 1985  
(manuscript received 29 Oct 84) pp 911-914

SMIRNOV, Ye. P., MIKHEYEV, A. O., GORDEYEV, S. K., KRASOVSKIY, A. N. and ALESKOVSKIY, V. B., corresponding member USSR Academy of Sciences, Leningrad Technologic Institute imeni Lensoviet

[Abstract] Experiments were conducted on synthetic diamonds and natural graphite having relative surfaces of 20 and 2  $\text{m}^2/\text{g}$  modified by the addition of titanium chloride groups. Titanium tetrachloride apparently forms  $-(\text{OTiCl}_2)$  and  $-(\text{OTiCl}_3)$  complexes at -OH groups on the diamond and graphite surfaces. Polymerization was carried out, directly after formation of the titanium groups, at atmospheric pressure in a n-heptane medium saturated with ethylene and then initiated with the addition of triethyl aluminum with a molar ratio of 10 to 100 in relation to the titanium groupings. The kinetic curve of the reaction on graphite showed a rapid drop in reaction speed to about one fiftieth of its initial value, apparently because the reducing

character of the graphite surface dropped the Ti to a lower, inactive oxidation state. The reaction curve on diamond showed an initial small rise and then a gradual drop of less than 50%. The steady portions of the curves showed similar  $E_a$  on the two surfaces--45 and 47 kJ/mole on diamond and graphite respectively. Infrared spectra of the polymers indicated a strongly linear character. At maximum concentrations of titanium groupings on the surfaces (4.2 mole/m<sup>2</sup> on diamond and 9.6 mole/m<sup>2</sup> on graphite), the polymers had an amorphous character. Lowering the surface titanium concentrations on the diamond 2.7 mole/m<sup>2</sup> yielded a more ordered polymer. These experiments indicate the possibility of tailoring the structure and composition of polymers implanted on solid surfaces. Figures 2; references 10 (Russian). [55-12672/12955]

UDC 678.044.678.742.2

#### PRODUCTION OF CATALYST FOR LOW PRESSURE POLYETHYLENE SYNTHESIS BY GAS-PHASE METHOD

Moscow PLASTICHESKIYE MASSY in Russian No 8, 1985 pp 7-9

BAULIN, A. A., CHERNYKH, A. I., SLAVINA, L. G., ABDULKHAKOVA, N. N., IVANOV, L. A. and GABUTDINOV, M. S.

[Abstract] An attempt was made to substitute a domestically produced starting material for the imported reagent in synthesis of the catalyst  $[(C_6H_5)_3SiO]_2CrO_2/SiO_2 + Al(OC_2H_5)_3(C_2H_5)_2$  used in the gas phase production of low pressure polyethylene (LPPE). It was shown that domestic [Soviet] silica gel and bistrifenylsilylchromate (BTSC) yielded a catalyst almost identical in its properties to one obtained from imported reagents. The LPPE synthesized over this domestically-prepared catalyst compared well with one produced over catalyst prepared from imported starting reagents.

References 9: 5 Russian, 4 Western.

[50-7813/12955]

UDC 678.632'32'21:678.643'42'5:546.18:66.018.4

#### THERMAL STABILITY OF PHENOL-FORMALDEHYDE AND EPOXYPHENOLIC POLYMERS WITH PHOSPHORUS-OXYGEN CONTAINING ADDITIVES IN SURFACE LAYER

Moscow PLASTICHESKIYE MASSY in Russian No 8, 1985 pp 15-17

MALYGIN, A. A., TRIFONOV, S. A., KOLTSOV, S. I., VINOGRADOV, M. V. and BARSOVA, V. V.

[Abstract] Thermal stability and combustibility of phenolformaldehyde spheres (PPS) and foam plastics PEN-1 containing phosphorus compounds in their surface layers were studied by the method of differential thermal

analysis and "fire tube" test. It was shown that the presence of phosphorus additives in the surface layer of the test materials increased their thermal stability by 140-150°C for PPS and by 40-50% for PEN-1. This shift towards higher temperatures was explained by chemical interaction of the phosphorus groups with reactive groups at the polymer surface forming P-O-P and P=O bonds which required higher energies for their reactions. Thus, it was shown that the fire retardants should be introduced in the surface layer for greater effect. Figures 2; references 6: 5 Russian (1 by Western author), 1 Western. [50-7813/12955]

UDC 678.742.2-134.442.2:621.792

#### EFFECT OF SOME TRIALKOXYSILANES ON ADHESIVE STRENGTH OF ETHYLENE-VINYL ACETATE COPOLYMER

Moscow PLASTICHESKIYE MASSY in Russian No 8, 1985 pp 17-18

KAKOVKA, T. N., VASILENKO, Ye. A., SALTANOVA, V. B. and RUMYANTSEV, V. D.

[Abstract] Organosilanes are used widely as primers for increased strength of polymer adhesion to inorganic substrates. The effect of silanes was investigated on the adhesive strength of ethylene-vinyl acetate copolymer [EVAC] used often in production of glues and adhesives. It was shown that the resistance to layering of the technical products was different from that obtained using silanes, after their vacuum distillation. This was due to the presence of alcohol and HCl in the technical product. The investigated silanes could be arranged in the following order of decreasing adhesive strength: aminopropyltriethoxysilane > vinyltriethoxyethoxy-silane > vinyltriethoxysilane > ADE > tetraethoxysilane. The adhesive bonding strength increased rapidly with the content of silane, reaching an asymptotic value with 0.5% of silane. The adhesive capability of these compositions could be altered by changing the conditions of silane hydrolysis. These data supported the proposition that there is a relationship between the rate of silane hydrolysis and its effectiveness in influencing the adhesive strength of the compositions. Figures 2; references 4: 1 Russian, 3 Western. [50-7813/12955]

UDC 678.743.678.664.678.674

#### PROPERTIES OF POLYURETHANE DERIVATIVES BASED ON TERNARY COPOLYMERS OF VINYL CHLORIDE, VINYL ACETATE AND VINYL ALCOHOL OBTAINED BY EMULSION AND SUSPENSION POLYMERIZATION

Moscow PLASTICHESKIYE MASSY in Russian No 8, 1985 pp 26-28

KUZNETSOVA, V. P., SIKORSKAYA, A. P., VALCHUK, T. A. and SHABALINA, O. G.

[Abstract] Ternary copolymers of vinyl chloride (VC), vinyl acetate (VA) and vinyl alcohol (VAL) obtained by emulsion polymerization are used widely

in the production of recording tapes. In an attempt to explore the possibility of using such ternary copolymers, obtained by suspension polymerization, in preparation of polyurethanes (PU), the reaction of isocyanate poly-addition of both types of polymers was studied. Also, the effect of ternary copolymers on the formation process, on the physical-chemical and protective properties was studied. It was shown that these ternary copolymers obtained by suspension polymerization had a narrow temperature range of decomposition, in contrast to the emulsion type copolymers. This could indicate homogeneous composition of such copolymers. The use of these copolymers in production of polyurethane covers would assure a complex of physical-mechanical and protective properties of these films. Figure 1; references 7: 6 Russian, 1 Western.

[50-7813/12955]

UDC 678.743.21.049

#### PLASTICIZING POLYVINYLCHLORIDE WITH 1,10-DECANEDICARBOXYLIC ACID ESTERS

Moscow PLASTICHESKIYE MASSY in Russian No 8, 1985, pp 42-23

MERZLIKINA, V. P., BARASHKOV, O. K., KIRILOVICH, V. I., CHEKHOVSKAYA, N. V.  
and RYZHAKOVA, L. V.

[Abstract] In order to expand the assortment of frost-resistant plasticizers for polyvinyl chloride (PVC), plasticizing action of a number of 1, 10-decanedicarboxylic acid (1,10-DCA) esters was studied, determining the temperature of PVC solution in the plasticizer ( $T_p$ ) and the solubility parameter ( $\delta$ ). It was shown that with increased number of methyl groups in the plasticizer, the  $T_p$  of PVC is raised from 383 to 443 K, while  $\delta$  is decreased. The thermodynamic parameter X of PVC interaction with plasticizer was calculated, showing that, with increased length of the alkyl radical, the X parameter is increasing. From thermodynamic considerations, it became apparent that plasticizing activity of 1,10-DCA could be obtained in esters with the alcohol radical length of  $C_4$  to  $C_8$  only. Indeed, PVC films obtained with such plasticizers showed good frost-resistance. Figure 1; references 5: 4 Russian, 1 Western.

[50-7813/12955]

UDC 678.674'.41'5:628.543

REPURIFICATION OF EFFLUENT IN PRODUCTION OF POLYCARBONATE

Moscow PLASTICHESKIYE MASSY in Russian No 8, 1985 pp 49-51

FISHMAN, G. I., PEVZNER, I. D., MELENTYEVA, N. D., LYUTIKOVA, N. N., SOROKIN, Yu. N. and MONAKHOVA, T. I.

[Abstract] Effluent forming in production of polycarbonate is separated into two streams: an acid and a basic stream. The basic portion contains 100--150 g/l of NaCl, admixtures of sodium bicarbonate and organic compounds: phenol or p-tert-butylphenol, acetone, methylene chloride and triethylamine. The acid component contains the same organic materials, phosphoric acid and traces of mineral salts. NaCl could easily be used in production of chlorine or in regeneration of cationic filters. A purification method was evaluated designed to recycle the effluent: the volatile components were evaporated and the salt solution was neutralized and passed through a sorption column of KU-2 cation exchange resin in the H<sup>+</sup> form. It was shown thus-purified effluent of the second stream could be used in preparation of rinsing solutions and in final washing of polycarbonate varnish during anion exchange demineralization. Figures 2; references 6 (Russian).

[50-7813]

UDC 678.744.32:66.095.3

PRODUCTION OF POLYACRYLATES IN HIGH BOILING SOLVENTS BY ACCEPTOR-CATALYTIC POLYCONDENSATION

Moscow PLASTICHESKIYE MASSY in Russian No 8, 1985 p 54

KHARAYEV, A. M., MIKITAYEV, A. K. and SHUSTOV, G. B.

[Abstract] In contrast to normally-used conditions for acceptor-catalytic polycondensation, polyacrylate synthesis was performed in high boiling solvents (diphenyl oxide, ditolylmethane) at 323-333 K for 1 hr. Then the temperature was elevated to 543--473 K for another hour to remove triethylamine hydrochloride. Thus a simplified synthesis of such polyacrylates was developed avoiding a purification step to remove low molecular byproducts. References 3 (Russian).

[50-7813/12955]

UDC 678.742.2.048

NEW POLYETHYLENE PHOTO-STABILIZERS

Moscow PLASTICHESKIYE MASSY in Russian No 8, 1985 p 57

KULIYEV, A. M., SARDAROVA, S. A., AGAMALIYEVA, M. M. and DZHAFAROV, A. S.

[Abstract] Derivatives of aromatic hydroxyketones retard the photo-aging processes of polymers. Compounds of the 3,4-dihydro-1,3-benzoxazine class are good non-staining photo-stabilizers of polyethylene (PE). A series of such compounds was obtained by condensation of respective 4-hydroxyacetophenones with formaldehyde and aniline derivatives in alcohol at 40-60°C, from which 3,4-dihydro-3-(aryl)-6-acetyl-1,3-benzoxazines were found to be the most effective photo-stabilizers. Reference 1 (Russian).  
[50-7813/12955]

UDC 678.743.22:553.625+678.046.3

PYROLYSIS OF PVC AND PVC + PHOSPHO-GYPSUM COMPOSITES

Moscow PLASTICHESKIYE MASSY in Russian No 8, 1985 pp 58-59

NORMETOV, L. T. and ARIPOV, E. A.

[Abstract] The effect of phospho-gypsum (a byproduct in the production of phosphoric fertilizers) on pyrolysis of polyvinyl chloride (PVC) and PVC + phospho-gypsum composites was studied. The investigation was carried out on the basis of a derivatograph of the system "Paulik-Paulik-Erdey" using a 2.5-20°C per minute heating rate. The data obtained showed that the phospho-gypsum undergoes dehydration during the preparation of the mixture under conditions resembling those used in production of linoleum where phospho-gypsum is used instead of asbestos. This substitution improved the sanitation-hygienic and health protective properties of linoleum. Thus it was shown that phospho-gypsum belongs to the class of active fillers with properties of antipyrenes. Figure 1; references 8 (Russian).  
[50-7813/12955]

UDC 678.742.2.046:669.14:539.61

ADHESION KINETICS OF POLYOLEFINS TO STEEL IN CONTACT THERMOOXIDATION.  
PART 5. FORMAL KINETICS IN THE DESCRIPTION OF RESISTANCE TO EXFOLIATION  
IN RELATION TO CONTACT TIME OF DICUMYL PEROXIDE-MODIFIED POLYETHYLENE

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHIMICHESKAYA  
in Russian No 4, 1985 (manuscript received 13 Feb 85) pp 442-448

KALNINSH, M. M., KAPISHNIKOV, Yu. V. and AVOTINSH, Ya. Ya., Riga Polytechnic  
Institute imeni A. Ya. Pelshe

[Abstract] Experimental data on polyethylene-steel adhesive processes were subjected to formal kinetic analysis to determine the relationship between resistance to peeling ( $A$ ) and the duration of thermooxidative contact time ( $t$ ). Data for dicumyl peroxide-modified polyethylene were obtained for the temperature range 423-483°K, with the peroxide concentration ranging from 0 to  $2 \times 10^{-2}$  weight fraction. Determinations of the rate constants of  $A$  with temperature showed an energy of activation of 37.7 kJ/mole, with  $A_{t=0}$  increasing proportionally to an increase in the concentration of the peroxide and the temperature. The latter phenomenon was ascribed to increased cross-linking in the polymer. These observations indicate that addition of organic peroxides to the polymer enhances thermooxidative crosslinking and, as a consequence, raises the values of  $A$ . Figures 5; references 8 (Russian).  
[71-12172/12955]

UDC 678.5.057.745:539.4

STRAIN HARDENING OF PLASTIC MOLDING MACHINE ELEMENTS

Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 9, Sep 85  
pp 23-24

LESHCHENKO, M. I., candidate of technical sciences

[Abstract] Studies were conducted on improving the wear resistance of machine elements used in molding plastics such as polystyrene, capron B, polyamide P68, and glass-filled polyamide SP68. The analysis demonstrated that optimal wear resistance was obtained with augers manufactured from nitrided 38Kh2MYuA steel, and cylinders prepared from boronized steel 45. The use of such methods for strain hardening of the machine elements at the Khmelnitski Plastics Industrial Association has resulted in an annual savings of more than 30,000 rubles. Figures 1.  
[98-12172/12955]

ADHESION KINETICS OF POLYOLEFINS TO STEEL IN CONTACT THERMOOXIDATION.  
PART 4. CORRELATION BETWEEN MACROMOLECULAR TRANSFORMATION AT CONTACT  
THERMOOXIDATIVE SITES AND RESISTANCE TO EXFOLIATION OF POLYOLEFIN-STEEL  
ADHESIONS

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHMICHESKAYA in  
Russian No 4, 1985 (manuscript received 13 Feb 85) pp 435-441

KALNIN, M. M., OZOLINSH, Yu. L. and MALERS, Yu. Ya., Riga Polytechnic  
Institute imeni A. Ya. Pelshe

[Abstract] Techniques previously described [this publication, No 5, pp. 564-571, 1983] were used to assess the kinetics of polyolefin-steel adhesion and in relation to the thickness of the polymer layer. Studies with polyethylene and vinyl acetateethylene copolymer demonstrated that oxidative crosslinking prevailed in the polymer layers immediated adjacent to the interphase boundary on contact thermooxidation in the temperature range of 423-473°K. This effect was ascribed to the catalytic effects of steel. Polyethylene and the copolymer layers that were more distant to the interphase evidenced destructive processes. Analysis of molecular weight distribution of the polyolefins across the thickness of the films indicated that exfoliative processes were predicated on the relationship between crosslinking and destructive processes. Figures 6; references 16: 14 Russian, 2 Western.  
[71-12172/12955]

STEREOREGULATORY EFFECTS OF TRICHLOROETHYL PHOSPHITE AS PROMOTER IN  
STEREOSPECIFIC POLYMERIZATION OF PROPYLENE

Moscow KINETIKA I KATALIZ in Russian Vol 26, No 4, Jul-Aug 85  
(manuscript received 3 Jan 84) pp 842-846

BIKUSHEV, G. S. and PETROVA, V. F., Kazan Institute of Chemical Technology  
imeni S. M. Kirov

[Abstract] The stereoregulatory effects of trichloroethyl phosphite (TCEP) as a promoter for  $Al(C_2H_5)_2Cl \cdot TiCl_3$  catalyst in stereospecific propylene polymerization was assessed in terms of kinetics and yield of isotactic and atactic fractions. The effects of TCEP and its molecular adduct with  $TiCl_3$  differ in that in the former case stereoregulation is accompanied by loss of catalytic efficiency, while in the second case the yield of the isotactic fraction increases. The differences between TCEP and the molecular adduct  $TiCl_3 \cdot P(OCH_2CH_2Cl)_3$  are primarily due to the nature of their interaction with stereospecific growth sites on the macromolecule, with antecedent combinations of  $TiCl_3$  and TCEP and with  $TiCl_3 \cdot P(OCH_2CH_2Cl)_3$  leading to irreversible inactivation. Thus, there appears to be no direct addition of

$P(OCH_2CH_2Cl)_3$  to the Ti-Cl bond. The complexed stereoregulator appears to be chemisorbed to some other site, and its coordination relative to the active sites represents a subsequent event. Figures 4; references 6: 5 Russian, 1 East German.  
[75-12172/12955]

UDC 678.664:547.497

## SYNTHESIS OF CATION-ACTIVE POLYURETHANE SEMICARBAZIDES

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 8, 1985  
(manuscript received 16 Apr 84) pp 882-885

SHEVCHENKO, V. V., PROTASOV, N. V., SHRUBOVICH, V. A. and VILENSKIY, V. A., Institute of Chemistry of High Molecular Weight Compounds, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Cation-active polyurethane semicarbazides were synthesized using as quaternary ammonium compounds the halides of  $N[1(2\text{-hydroxyethyl})\text{hydrazino-} \text{carbonylmethylene}]$  pyridinium. The resultant products consisted of segmental copolymers with flexible regions consisting of oligohydroxytetramethylene-glycol segments and rigid segments of urethane and 2-N-substituted semicarbazide. The side chains of the rigid segments consist of pyridinium halide radicals differing in the nature of the anion (Cl, Br or I). In many respects the products with  $Br^-$  possessed superior characteristics in comparison with the other halide ions, including the highest resistance to breakage ( $\sigma = 41.8$  MPa) on stretching ( $\epsilon = 1400\%$ ). The temperature of decomposition of these products was in the 190-210°C range, markedly below that (260°C) for the nonionic analog. The cation-active copolymers were soluble in amide solvents and DMSO, and insoluble in alcohols, hydrocarbons and other common solvents. Figures 1; references 5: 3 Russian, 2 Western.  
[045-12172/12955]

UDC 541.11

## MODIFICATION OF POLY-(4,4'-DIPHENYLETHER)-PYROMELLITIC ACID WITH ACETYLACETONATES OF TRANSITION METALS

Minsk VESTNIK AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIH NAUK in Russian No 4, 1985 (manuscript received 5 Aug 83) pp 86-89

VOLOZHIN, A. I., KRUTKO, E. T., ROZMYSLOVA, A. A. and SHISHKO, A. M., Institute of Physical Organic Chemistry, BSSR Academy of Sciences

[Abstract] Acetylacetones of  $Cu^{2+}$ ,  $Fe^{3+}$ , and  $Al^{3+}$  were reacted with poly-(4,4'-diphenylether)-pyromellitic acid (PDP) in dimethylformamide. Reaction enthalpies were first measured at  $25 \pm 0.001^\circ C$  for the reaction of

4,4'-diaminodiphenyloxide with the dianhydride of pyromellitic acid in dimethylsulfoxide, dimethylacetamide, dimethylformamide and N-methylpyrrolidone. The enthalpies differed significantly in the various solvents, but they all produced smooth thermal emission curves, indicating that the synthesis of PDP proceeded by a similar mechanism regardless of solvent. The resulting PDP was reacted with the metal acetylacetones. Aluminum gave the highest reaction enthalpy (18.9 kcal/mole), iron the lowest (8.0 kcal/mole) and copper near it (9.3 kcal/mole). These apparently formed polymeric coordination complexes whose structure and stability depended upon the metal ion involved. Heats of solution indicated a two-stage mechanism of formation, with the metal compounds first complexing with the solvent and then the PDP interacting with this intermediate complex. Viscosity measurements of solutions in dimethylsulfoxide of the Cu and Fe-PDP complexes over time at 5° C showed a rise of viscosity during the first day and then a gradual decline, but at a faster rate than unmodified PDP. A probable explanation is the gradual breakup of the metal complexes and of the PDP itself. Figures 3; references 5 (Russian).

[29-12672/12955]

UDC 541.64:539.3+678.7

#### ANTISTATIC TREATMENT OF INFUSION COPOLYMERS OF POLYETHYLENE WITH ACRYLIC ACID

Minsk VESTNIK AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIKH NAUK in Russian No 4, 1985 (manuscript received 20 Apr 83) pp 83-86

KRUL, L. P., BRAZHNKOVA, L. Yu., KUMACHEV, A. I., POLYKARPOV, A. P. and OSIPENKO, I. F., Scientific Research Institute of Physical Chemical Problems, Belorussian State University imeni V. I. Lenin; Institute of Physical Organic Chemistry, BSSR Academy of Sciences

[Abstract] Polyethylene sheets 150  $\mu\text{m}$  thick were immersed in a 15% solution of acrylic acid in toluene and then subjected to 0.3 Mrad irradiation. One treatment produced a sheet with a  $\Delta R$  of 15.3% of the polyethylene mass [ $\Delta$  not expanded]. Repeating the treatment a second and third time with fresh monomer solutions gave sheets with  $\Delta R$  of 48.7% and 81.9% respectively. These treated sheets were further treated with a 5% emulsion of benzolsulfonates of methylethylaminomethyl derivatives of esters of higher fatty acids (alkali antistatic compound OS-2) or with a 5% solution of either quaternary ammonium salts of diethylaminomethyl derivatives of polyethylene glycol esters of alkylphenols (antistatic equalizer A) or sodium hydroxide. Sheets with a high  $\Delta R$  had a relative surface electrical resistance up to an order of magnitude below untreated sheets. Treatment with the surface-active compounds further decreased the resistance by another 3-5 orders of magnitude. However, washing with water sharply increased the resistance -- for samples with a low  $\Delta R$ , essentially restoring the originally resistance. For samples with  $\Delta R$  of 48.7% or higher, the sodium treatment also decreased the resistance by up to 5 orders of magnitude, a decrease which was not affected by continued washings. Lower concentrations of sodium hydroxide were less effective.

This lowering of resistance was apparently due to the presence of carboxyl groups on the surface of the polymer sheets. Results could possibly be changed significantly by changes in experimental conditions. Localized surface infusions might give good antistatic properties even at significantly lower  $\Delta R$ . References 12: 10 Russian, 2 Western (1 by Soviet authors including Osipenko and Krul).

[29-12672/12955]

## RADIATION CHEMISTRY

### DISCOVERY ON PHOTOCHEMICAL EFFECTS OF MAGNETIC FIELDS

Leningrad LENINGRADSKAYA PRAVDA in Russian 1 Nov 85 No 3

[Text] Encyclopedias tend to become outdated quickly in our age of scientific and technological progress. Physicists, chemists and biologists, for example, have long been concerned with the basic question: do magnetic fields affect chemical reactions? "The Concise Chemical Encyclopedia" (Kratkaya khimicheskaya entsiklopediya), which was published 20 years ago, answered this question in the negative. Recent research has disproved this generally accepted proposition, however.

A scientific discovery made by associates of the USSR Academy of Sciences' Institute of Chemical Physics was entered in the USSR State Register of Discoveries on October 31. Results of basic research by these scientists have demonstrated that an external magnetic field is capable of producing effects on photo processes in nonmetallic solids. Among them are polymers and plastics, for example.

Results of this basic work, which was done by Doctor of Physical-Mathematical Sciences Ye. L. Frankevich and Candidate of Physical-Mathematical Sciences Ye. I. Balabanov, are already being used in our country and abroad. On the basis of these results, modern methods and instruments have been developed for the study of chemical reactions that are utilized in photochemistry and radiation chemistry, for example.

FTD/SNAP  
/12955  
CSO: 1841/142

UDC 541.64.537.311

RADIATION-INDUCED ELECTRICAL CONDUCTIVITY IN  $\text{Fe}(\text{CO})_3$   $\pi$ -COMPLEXES WITH POLY(STYRENE-BUTADIENE) BLOCK POLYMER

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 284, No 5, 1985  
(manuscript received 6 Dec 84) pp 1174-1178

TYUTNEV, A. P., BRONSSTEYN, L. M., SAYENKO, V. S., ABRAMOV, V. N., VALETSKIY, P. M., POZHIDAYEV, Ye. D., VINOGRADOVA, S. V. and KORSHAK, V. V., academician, Moscow Institute of Electronic Instrument Construction; Institute of Hetero-organic Compounds, USSR Academy of Sciences, Moscow

[Abstract] In order to elucidate and define the effects of additives to radiation-induced electrical conductivity in polymeric systems, an analysis was conducted on induced conductivity in an Fe-containing block copolymer with the  $\text{Fe}(\text{CO})_3$  fragments located on the main polymer chain. Comparative studies on a control poly(styrene-butadiene) block copolymer demonstrated that 0.3 msec exposure to accelerated 65 keV electrons at 25 to 100°C induced a nonstationary electrical conductivity equivalent to  $2.3 \times 10^{-14} \text{ F.m}^{-1} \cdot \text{Gy}^{-1}$  when measured in a  $2 \times 10^7 \text{ V/m}$  electric field. The energy of activation for the slow component was measured at 0.38 eV. With 3.5, 5.0 and 11%  $\text{Fe}(\text{CO})_3$  the respective conductivities measured under identical conditions were  $0.7 \times 10^{-14}$ ,  $0.29 \times 10^{-14}$  and  $0.14 \times 10^{-14} \text{ F.m}^{-1} \cdot \text{Gy}^{-1}$ . In addition, the energy of activation of the slow component was 0.15 eV. Evaluation of the volt-ampere characteristics of the induced conductivity indicated that it was due to ion-pair mechanisms rather than free charges. Figures 3; references 12: 9 Russian, 3 Western.

[99-12172/12955]

UDC 678.742:539.317

RADIOTHERMOLUMINESCENCE STUDY OF AMORPHOUS PHASE ANISOTROPY OF THERMODEPOSITED LOW DENSITY POLYETHYLENE PREPARED BY RADIATION CROSSLINKAGE

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHMICHESKAYA in Russian No 4, 1985 (manuscript received 29 Nov 84) pp 425-434

KRESLINSH, E. V., Latvian State University imeni P. Stuchka

[Abstract] Radiothermoluminescence was used to study the amorphous phase of low density polyethylene crosslinked by radiation, leading to the observation that the energy of activation of the relaxation process responsible for the beta-maximum of luminescence is on the order of 70.4 kJ/mole. Mathematical analysis demonstrated that the intensity of luminescence evident with an increase in the transient chains of polyethylene in the amorphous phase is responsible for the temperature-dependent increase in the beta-maximum. The correlation observed between the temperature-dependent shift in the beta-maximum of luminescence and temperature-dependent strain of the polyethylene samples on isometric heating below the  $T_m$  indicates that both parameters can be used to assess changes in the amorphous phase. Figures 5; references 15 (Russian).

[71-12172/12955]

LASER-INDUCED CHEMICAL REACTION OF  $Na(3P) + HCl$  IN GAS PHASE

Moscow ZHURNAL EKSPERIMENTALNOY I TEORETICHESKOY FIZIKI in Russian Vol 42, No 2, 25 Jul 85 (manuscript received 29 May 85) pp 52-54

BORISOV, S. K., KRYNETSKIY, B. B., MISHIN, V. A., PROKHOROV, A. M. and STELMAKH, O. M., Institute of General Physics, USSR Academy of Sciences

[Abstract] A flow-through laser chemical reactor was used to study the kinetics of the  $Na(3P) + HCl \rightarrow NaCl + H$  process. The rate constant of the pseudofirst order reaction, when the metal concentration is much lower than that of the acid, was obtained from the kinetics of luminescence, the homogeneous transition state broadening and the intensity of the laser irradiation. Theoretical and literature experimental data were used to choose the experimental conditions: argon pressure 80 torr, Na vapor concentration  $10^{11}/cm^3$  and HCl concentration  $10^{13}-10^{14}/cm^3$ . The pseudofirst order rate constant obtained from the results was  $6-8 \times 10^4/cm^3 \cdot sec$  at an HCl concentration of  $7.5 \times 10^{13}/cm^3$ , linear with HCl pressure, corresponding to a bimolecular rate constant of  $0.66-1.20 \times 10^{-9} cm^3/sec$ . At the most probable rate of atom-molecule impact,  $9 \times 10^4 cm/sec$ , this leads to a cross section of  $100 \text{ \AA}^2$ , which is in good agreement with that found in the literature. Figures 2; references 7: 3 Russian, 4 Western.  
[359-12126/12955]

UDC 543/42

SPECTRAL-ISOTOPIC ANALYSIS OF NITROGEN AND CARBON IN DELIMITED AREAS OF VEGETATION SAMPLES USING LASER VOLATIZATION

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 40, No 8, Aug 85 (manuscript received 1 Nov 83) pp 1456-1469

LAZEYEVA, G. S. and MESHCHERYAKOVA, T. Yu., Leningrad State University imeni A. A. Zhdanov

[Abstract] Technical details are presented on the analysis of the isotopic composition of carbon and nitrogen in delimited areas of plant samples using either  $CO_2$  or Nd laser volatization. The resultant gas phase is then subjected to spectroscopic analysis on the basis of isotope dilution technology. Determinations of the isotopes  $^{15}N$  and  $^{14}N$  and  $^{13}C$  and  $^{12}C$  requires the presence of at least 1-2  $\mu g$  of each element in the area of analysis, which generally falls in the range of 0.3 to 1.5  $mm^2$ . More consistent results were obtained with the use of a continuous  $CO_2$  laser rather than pulsed Nd emission. Figures 5; references 9 (Russian).  
[048-12172/12955]

WATER TREATMENT

UDC 628.543

PROCESSING OF CONCENTRATED EFFLUENT DURING CONSTRUCTION OF CLOSED SYSTEMS OF INDUSTRIAL WATER SUPPLY

Moscow KHMICHESKAYA PROMYSHLENNOST in Russian No 8, 1985 pp 477-481

YAGODIN, G. A., BERNSTEYN, L. A. and MAKAROV, S. V.

[Abstract] Possible solutions are presented for one of the most complex problems in formation of closed systems of industrial water supply--processing of concentrated effluent and processing of concentrated salt solutions forming in the process of recirculating water treatment. The paper concentrates on two sub-topics: regeneration of waste etching acid solutions during formation of local semicirculating systems of industrial water supply and processing of concentrated salt solutions in formation of recirculating water supply systems. In general, concentrated effluent will always contain some impurities. Therefore, in development of the system for processing of effluent, the isolation of impurities must be considered in light of their possible utilization in future processes, in light of water recirculation or recirculation of the technological solutions. In general, the problem must be approached on a case-by-case basis. References 16: 14 Russian, 2 Western. [61-7813/12955]

UDC 612.8

OXIDATION OF HYDROXYZOBENZENE IN AQUEOUS SOLUTIONS

Kiev KHIMIYA I TEKHNOLOGIYA VODY in Russian Vol 7, No 4, Jul-Aug 85  
(manuscript received 27 Oct 83) pp 15-17

KERZHNER, B. K., TARAN, P. N. and SHEVCHENKO, M. A., Institute of Colloid Chemistry and Water Chemistry imeni A. V. Dumanskiy, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Studies were conducted on the effectiveness of ozone in the oxidation of the o- and p-isomers of hydroxyzobenzene in aqueous solutions. The course of oxidation was followed by TLC, GLC and spectroscopic techniques.

The essential conclusions were that the oxidative process involved bond disruption between the aromatic ring and the azo group, followed by opening of the aromatic ring. The latter process yielded low MW aliphatic aldehydes. In addition, intermediate products identified in the oxidation of hydroxyazo-benzene by ozone included phenyl diazonium salt and phenyl diazyl radicals. Figures 1; references 6: 3 Russian, 3 Western. [73-12172/12955]

UDC 628.162

#### REACTION OF NITROPHENOLS WITH ACTIVE CHLORINE IN DILUTE AQUEOUS SOLUTIONS

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 7, No 4, Jul-Aug 85  
(manuscript received 5 Jul 84) pp 17-21

VAKULENKO, V. F., TARAN, P. N., SHEVCHENKO, M. A. and MILYUKIN, M. V., Institute of Colloid Chemistry and Water Chemistry imeni A. V. Dumanskiy, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Studies were conducted on the reaction of chlorine water with 4-nitrophenol, 2,4- and 2,5-dinitrophenols, 2,4,6-trinitrophenol and 2-methyl-4,6-dinitrophenol (I) over a pH range of 1.2-11.0. Analysis of the kinetics showed that the rate of decomposition of the nitrophenols was greater in acid media than in neutral media. The decomposition was particularly efficient in 0.1 M hydrochloric acid, i.e., under conditions in which chlorine hydrolysis was completely inhibited. The presence of an electron donor substituent, e.g., in I, markedly enhanced the rate of nitrophenol decomposition. Electron acceptor groups had the reverse effect. At alkaline pH, e.g., pH 11.00, only I was decomposed to a measurable extent. The data were in agreement with a radical chlorination mechanism of action leading to extensive destruction of the nitrophenols. However, the formation of volatile organo-chlorine compounds in the process limits the use of chlorine in the treatment of water for the elimination of nitrophenol derivatives. Figures 4; references 8: 5 Russian, 3 Western. [73-12172/12955]

SOLUTE EFFECTS IN REVERSE OSMOSIS TREATMENT OF WASTE WATERS FROM SULFATE-CELLULOSE PLANTS

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 7, No 4, Jul-Aug 85  
(manuscript received 21 Mar 83; in final form 20 Mar 84) pp 21-25

TERPUGOV, G. V., DYTNERSKIY, Yu. I., SEMENOV, V. P. and SOBAKIN, V. M.,  
Moscow Institute of Chemical Technology imeni D. I. Mendeleyev; All Union  
Scientific Research Institute of Cellulose and Paper Industry, Leningrad

[Abstract] An analysis was conducted on the effects of solute concentration in waste waters of sulfate-cellulose plants on the efficiency of reverse osmosis water treatment. The quantitative studies were conducted in terms of  $\text{Na}^+$  concentrations in the treated water and filtrate, since this ion represents both the degree of pollution (with  $\text{Na}_2\text{SO}_4$ ) and degree of purification. Evaluation of the results with cellulose acetate and 'dynamic' membranes demonstrated that an increase in the concentration of the dissolved substances ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , lignin, sugars, alcohols, etc.) in the waste water increases the osmotic pressure and thereby diminishes the efficiency of reverse osmosis. In addition, the increased solute concentration increases the viscosity which may also contribute to deposit formation on the separatory membrane, particularly in the case of sulfate-containing waters. Figures 5; references 14: 12 Russian, 2 Western.

[73-12172/12955]

ELECTROCHEMICAL OXIDATION OF ORGANIC DYES IN AQUEOUS SUSPENSIONS OF  $\text{MnO}_2$

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 7, No 4, Jul-Aug 85  
(manuscript received 27 Sep 83) pp 35-38

MUMINA, O. A. and MATSKEVICH, Ye. S., Institute of Colloid Chemistry and Water Chemistry imeni A. V. Dumanskiy, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A comparative study was conducted on the efficiency of chemical and electrochemical means of oxidation of organic dyes with a view toward the use of such systems in water purification. The studies were conducted with model systems of aqueous suspensions of  $\text{MnO}_2$  (16 g/liter) in distilled water with  $\text{NaCl}$  or  $\text{Na}_2\text{SO}_4$  to a concentration of 0.05 g-equiv/liter. Following oxidation, the filtrates were analyzed in photocalorimeters at 540 or 490 nm. Studies with peat extracts and triphenyl methane dyes showed that 100% elimination of the dyes was achieved with anodal oxidation on platinum electrodes with  $i = 20 \text{ mA/cm}^2$  after 3.5 min. Maximal effectiveness of electrochemical purification was obtained in the pH range of ca. 7 to 9. The removal of the organic pollutants was ascribed to adsorption on the  $\text{MnO}_2$  particles as the initial step, which in turn facilitated their subsequent

oxidation by the products of water electrolysis (e.g., radicals, active atoms of oxygen, etc.) The electrochemical approach was also found to be much more efficient than the use of chlorine or hydrogen peroxide. Figures 4; references 5 (Russian).

[73-12172/12955]

UDC 541.18.041:622.794.2

#### FLOCCULATION TREATMENT OF RECIRCULATING WATER FROM COAL PROCESSING

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 7, No 4, Jul-Aug 85  
(manuscript received 2 Sep 83) pp 38-42

BAYCHENKO, A. A., BARAN, A. A., MITINA, N. S. and NALEPA, V. F., Kemerovo Polytechnic Institute; Institute of Colloid and Water Chemistry imeni A. V. Dumanskiy, Ukrainian SSR Academy of Sciences, Kiev; Berezovskaya Central Enrichment Plant, Berezovskiy

[Abstract] Trials were conducted on the efficiency of several flocculating agents in the treatment of recirculating water at a coal processing plant, in order to devise an optimal treatment scheme. Three flocculants (anionic polyacrylamide, nonionic polyethylene glycol, high MW cationic polyelectrolyte VPK-101) were tested on coal and clay suspensions in relation to the presence of stabilizing ( $K^+$ ,  $Na^+$ ,  $HCO_3^-$ ; 380-400 mg/liter) and coagulating ( $Ca^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ ; 200-220 mg/liter) ions. Polyacrylamide lost effectiveness in the presence of stabilizing ions, with recovery of some flocculation on supplementation with the coagulation-promoting ions. The stabilizing ions had virtually no adverse effects on the flocculant activity of polyethylene glycol or VPK-101. Flocculation was improved by pre-treatment with  $Al_2(SO_4)_3$ , which reduced the stability of the suspensions under study. On the basis of these findings, a one step flow scheme for the purification of recirculating water at coal processing plants is described. Figures 4; references 7 (Russian).

[73-12172/12955]

UDC 778.588:628.543+77.027.3

#### RECOVERY OF SILVER FROM FILM PROCESSING WASTE WATER

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 7, No 4, Jul-Aug 85  
(manuscript received 11 Aug 83) pp 48-50

IVANOVA, L. S., GRABCHAK, S. L. and KRICHESKAYA, G. V., Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Five synthetic ion-exchange resins and activated charcoal were tested for their efficiency in silver recovery from film processing waste

water. In column adsorption studies at pH ca. 6 the adsorbents ranked as follows in adsorptivity of silver: EDE-10P > AN-2F > AV-16 > VP > AV-17 > activated charcoal. Filtration of the water through activated charcoal enhanced 2- to 3-fold the effectiveness of EDE-10P by removal of organic matter and particulates. Elution of the columns with a mixture of 3%  $\text{NH}_4\text{OH}$  and 4%  $\text{NH}_4\text{Cl}$  resulted in 100% desorption of the silver. For regeneration, EDE-10P was washed with 0.05-1 M  $\text{H}_2\text{SO}_4$  to pH ca. 2, followed by a water wash to pH ca. 5-6. Figures 1; references 7 (Russian).  
[73-12172/12955]

UDC 547.973.3-628.356

#### DETERMINATION OF ADENOSINE TRIPHOSPHATE IN ACTIVATED SLUDGE

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 7, No 4, Jul-Aug 85  
(manuscript received 28 Mar 83) pp 56-58

SMIRNOVA, L. A., FILENKO, S. N. and SHCHETININ, A. I., Ukrainian State Planning and Scientific Research Institute of Municipal Constructions, Kharkov

[Abstract] A relatively rapid and simple spectrophotometric method has been devised for the determination of ATP in activated sludge by a series of extractive and precipitating steps. The initial step consists of nucleotide extraction with boiling distilled water, elimination of proteins by acidification with  $\text{HClO}_4$ , and precipitation of the nucleotides with barium acetate. The precipitate is subsequently washed with distilled water and hydrolyzed with 0.1 M HCl. The precipitate formed on addition of  $\text{Na}_2\text{SO}_4$  is removed by centrifugation, and the supernatant is analyzed for ATP from OD at 260 nm. Comparison of results obtained by spectrophotometric analysis and analysis of phosphorus before and after hydrolysis showed excellent agreement, indicating that this approach constitutes a convenient nonenzymatic method of ATP determination in activated sludge. Figures 2; references 9:  
7 Russian, 2 Western.  
[73-12172/12955]

AUTOMATION OF INSTALLATIONS FOR TREATING WATERS POLLUTED WITH LUBRICATING COOLANT LIQUIDS

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 7, No 4, Jul-Aug 85  
(manuscript received 19 Apr 83) pp 73-75

NAZARYAN, M. M., YEFIMOV, V. T., KULSKIY, L. A. and YESAULOV, S. M., Kharkov Polytechnic Institute imeni V. I. Lenin; Institute of Colloid Chemistry and Water Chemistry imeni A. V. Dumanskiy, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A schematic is presented of an automated installation for the electrochemical treatment of water polluted with lubricating coolants. The water is collected into a settling tank for the removal of metallic and abrasive particles as the first step in the process. The clarified water is then passed into a mixing and neutralizing tank for treatment with HCl and mixing with compressed air to adjust the pH to 5.0-5.7. The following step involved gravity flow to the electrolyzer for the removal of emulsified oil, with the oil-bearing waste transferred to a sludge collector. The treated water is then transferred to another settling tank, from which a portion of the water is returned as an electrolyte to the electrode chamber for electrocoagulation. This scheme assured 99.0% removal of the lubricating coolants in trial runs, yielding water with a chemical oxygen demand of 240-350 mg O<sub>2</sub>/liter and a pH of 6.8-7.3. Figures 2; references 7:

6 Russian, 1 Western.

[73-12172/12955]

SHORTCOMINGS OF PULP AND PAPER INDUSTRY

Moscow IZVESTIYA in Russian 23 Jun 85 p 2

[Article by V. Sukhachevskiy: "Prime Cost of Style. Why the Pulp and Paper Industry is Lagging"]

[Text] You don't have to be an economist to know this: If money is put into some industry or other, that means it is done to develop it, to obtain a higher result than before. And the renovation of production, naturally, should pay for the expenses.

But what if this doesn't happen? If the funds--and a great deal of them--are spent, but the returns do not follow? Moreover, not in one production facility taken individually, but in the sector as a whole?

Almost 10 years ago, in 1976, it was decided to develop the pulp and paper industry. Technical reoutfitting of its enterprises began. Major capacities were started up in Syktyvkar Lumber Industrial Complex, and combines in Svetogorsk, Kondopoga, and Balakhna. A highly productive machine of Soviet design was started up in Zhidachev Combine. In all, during this time new capacities to produce 230,000 tons of newspaper grade and 220,000 tons of printing grade paper were introduced. In other words, the preconditions were created so that our publishing houses could work smoothly.

The preconditions were there, but the sector was unable to realize them. While the output of newspaper grade paper was growing, if slowly, the production of paper for books and journals actually decreased compared to 1976. For example, 10 years ago Leningrad Paper Factory No 1 produced 45,000 tons per year, but last year only 8,000. What happened? Everything is simple. The residents of Leningrad, concerned for the cleanliness and aesthetic appearance of their native city, proposed eliminating the raw materials shop in the factory. The ministry agreed with the arguments and promised to ensure local production using raw materials brought in from Bratsk. But the promise remained just a promise, and the paper workers were on starvation rations.

Leaders of the sector frequently explained losses of productivity by the shortage of raw materials. This reason is cited, for example, to justify the reduced productivity--by 35,000 tons--in Kamskiy Combine, although it is located in one of the largest raw lumber regions of the country.

Unfortunately, this enterprise is a classic example of unbalanced production. The capacity of the raw lumber base does not satisfy the needs of the paper-making machines. In similar relations of disharmony, as the specialists say, are wood-pulp and cellulose production, pulp and paper-making capacities, technological processes and refining buildings, and the demand for manpower and the possibility of housing it.

Obviously, all these disproportions did not form overnight. Enterprise director A. Skachilov and Chief Engineer G. Parshikov assert that when they took over the combine they were immediately hit in the face by its wretched "dowry." But the doubts were extinguished by a promissory note given by leaders of the sector: it was planned to bring order to the enterprise within a short time. And in fact, the USSR Ministry of Timber, Pulp and Paper and Wood-Processing Industry undertook a program of radical reconstruction in Kamskiy Pulp and Paper Combine. This program was to embrace all production--from preparing the raw materials to turning out the finished product. But, as later became clear, the ministry made a basic error: it failed to match good impulses with actual capacities.

This is what came of that. In March of this year, Kamskiy Combine produced 10 million square meters of paper above the plan. Good? For whom, though? Leaders of the enterprise, for example, fell under the press of ministerial rebuke. Because, by fully loading their paper-making machines, the combine was unable to fulfill the target for producing marketable pulp--that is, it was not supplying it to other enterprises. From the ministry came the demand: hand over the full volume of marketable pulp and your machines can wait.

I will return again to this question, but for now let me note: the Kamskiy Paper Workers are not alone in attempting to eliminate difficulties which come down to them "from above." This can be confirmed, for example, in Zhidachov Combine in Lvov Oblast. You couldn't call the situation in which it finds itself anything other than anecdotal material. Here, as we have already noted, new capacities were established. But instead of the 30,000 tons of typographic paper which was earlier produced, last year the combine turned out a total of...1,000 tons. The raw materials are brought here directly from Sakhalin. Brought with stoppages, great expenses, and losses.

Often, very often, we hear that some manager or other, explaining the reasons for failures, blames the subcontractors for everything: one failed to make the deliveries, another delayed them, a third made the deliveries but they were of poor quality. And then this manager sighs wistfully: if only, he says, everything was in one pair of hands, then there would be order....

Workers in the USSR Ministry of Timber, Pulp and Paper, and Wood-Processing Industry are not able to dream this dream. They have everything in their hands. It seemed obvious that the combination of two sectors into one--timber and wood processing, and pulp and paper--which occurred several years ago, would make it possible to better organize integrated operation of the entire large business connected with using timber resources. Then why are paper workers nearly always complaining about the shortage of raw materials? After all, their own dear timber ministry is conducting matters, not the ministry, say, of energy or coal industry.

However, the USSR Ministry of Timber, Pulp and Paper, and Wood-Processing Industry has recently become ashamed to blame the raw materials: it is a bit awkward to say that there is not enough timber when the timber is yours. But there are subcontractors from other departments, is it possible to attribute the blunders to them? This tactic, frankly, has more than once come to the aid of "quick-witted" managers. It has been used as a weapon in the timber department as well. They ask: Why isn't the production of paper growing? They answer: Well, how can it grow, if there isn't enough energy, fuel, and cars?

And in general there are no arguments. Facts? Please! In Solikamsk Combine the energy has more than once or twice been shut off without warning--and the production is continuous.... Kondoponga Combine is getting fewer cars than it needs. It's all the same, the subcontractors are not coming through, and can a sector even be found which has no complaints about subcontractors? It is all, I repeat, like that, but let us examine the complaints more carefully.

It is the fault of workers in energy and railroads that last year, according to approximate calculations, 37,000 tons of paper were not produced. (Why "approximate"? Because there has never been a true inventory in the ministry.) That is no small matter, of course. But as for the plan, it was underfulfilled by 118,000 tons! That is, you can in no way explain the lion's share of the losses as the effect of "outside factors," which the USSR Ministry of Timber, Pulp and Paper, and Wood-Processing Industry currently so loves to refer to.

And there is another important circumstance, in contrast, which the ministry does not like to dwell on. If we compare the energy and transportation provided to paper workers several years ago and now, we find that they are now getting a significantly greater total. The ministry might object: this is only natural, this sector today is not the same as it was before. And indeed the sector is not the same: having received more than 7 billion rubles in capital outlays over 10 years, the pulp and paper industry has not only not paid for the vast expenses by producing additional output, but, on the contrary, its work has deteriorated. In the past 6 years, failure to fulfill production plans for print quality paper has been a chronic problem; publishing houses each annually receive 100,000-120,000 tons of paper less than they are supposed to. (Unfortunately, using the paper which should have been produced in the last 6 years but was not produced, all of our typography and books being made could be taken care of for 15 months!).

The reduced volumes of production, however it may contradict logic, have brought along with them reduced quality of the paper. But this is only a contradiction at first glance. In a more careful examination of the problem, it is possible to see how the one depends directly on the other. The style developed by the leadership of the sector--to "pull out" the plan at any cost, what comes tomorrow is unimportant, tomorrow has not come yet--this style has not had a good effect and cannot have a good effect either in quantity or in quality.

Let us sum up briefly. With all the importance of the sector's production for the economy, I would like to focus readers' attention not so much on production

indicators, as to what lies behind the concept "production relations." In other words, to touch on a number of questions which might be of interest not only to paper workers but also to workers of other sectors. Because there are not and cannot be "timber" or "metallurgy" styles and methods of administration.

It is undeniable that the poor work of the pulp and paper industry is partly due to the effect of outside factors. We have tried to show this. But, I repeat, only partly. Workers in the ministry, however, are inclined to turn everything upside down, considering what is secondary to be central, and what is central to be secondary. Meanwhile, back in the distant days when the Ministry of Timber, Pulp and Paper, and Wood-Processing Industry did not yet exist, the practice of finding the mote in the eyes of others while not seeing the beam in one's own eye was condemned. As for the beam--in this case, that is quite precise. For example, the Krasnoyarsk Pulp and Paper Combine has long been in the company of the laggards. And how do they explain this situation there? Don't be surprised: everything is piled up on the severe winter and the shortage of beams.

"You just have to wonder," observes combine worker V. Biryukov. "In Siberia the winters are always cold, but at least complaining about the shortage of timber is not serious--we are in the center of a heavily wooded area. It seems to me that the main thing which is causing shortcomings is the uncritical attitude toward business, self-satisfaction, and unwillingness to take note of mistakes."

The worker's conclusions are confirmed by an assessment which resounded at the Krasnoyarsk Gorkom Plenum in 1983: "The party committee of the combine is unable to concentrate on the main problems and bring their resolution to completion. Instead of vital organizational work there is a unified outside appearance and bustling about without results...."

Let us glance into the "kitchen" of the enterprise--lumber exchange. The disorder which prevails there has long been known to everyone. More than once the workers have reported on it to the party committee. But its secretary, Sh. Molyshev, has done everything possible in order to "not notice" the critical signals. The indifferent attitude toward disorder in lumber exchange led to a situation in which a fire occurred which wiped out tens of thousands of cubic meters of wood.

There are many such instances. But I will return to the problems which are disturbing the collective of the Kamskiy Pulp and Paper Combine. Leaders of the enterprise have this proposal: without stopping the production of paper, to make capital repairs on the cookers.

The combine is asking the ministry to give it 2 years for this. The condition: to plan for the enterprise an output of pulp "minus one cooker." Within 2 years the collective is obliged, without reducing the rate of paper production, to bring the cooking equipment into a state of order. After this it would be able to supply pulp completely both for itself and for subcontractors. But no reaction followed this proposal. It is as if it never happened. And perhaps the ministry simply brushed it off: why bother with advice? It only interferes with work.

This proposal would not have been decided upon if it were based only on hypothetical arguments. But here is a telling fact. Technical engineer V. Chervasov, in a letter to the editorial office of the newspaper LESNAYA PROMYSHLENNOST, proposed, in his view, a successful resolution to the problem of constructing timber roads which would be usable year-round. The question is extremely urgent and it is fully natural that the editorial office introduced him to leaders of the sector. And then what? First Deputy Minister G. Medvedev snapped back in a letter: "Only professional letters should be directed to the leadership, send amateur ones back to the authors." It is not surprising that this same attitude toward the advice and suggestions of working people has begun to take root also in certain enterprises of the sector.

Having become convinced for some reason or other of the infallibility of their words and actions, workers in the ministry receive critical observations directed to them in an unhealthy fashion. Moreover, they are frequently inclined to see successes even in places where something has turned out to be a failure. The party committee of the ministry, unfortunately, also suffers from this "color-blindness." Its secretary, V. Ovchinnikov, giving a paper at a report-election party conference, spoke heartily about major advances in the sector, and the raised level of administration in its staff. But the opinion of delegates to the conference was diametrically opposed. They announced directly that the level of work in the ministry does not meet the requirements of the times. The sector has gotten into great debt with the government, failing to fulfill targets for deliveries of commercial wood, pulp, cardboard, paper for the press, and many other forms of production. They also cited reasons for this, including some such as shortcomings in the selection, placement, and indoctrination of cadres. It was noted in particular that the ministry is not being persistent enough in eliminating instances of bureaucratism and red tape, and untimely and formal perusal of the letters and requests of working people. At the same time, every year the headquarters of the sector sends out hundreds of thousands of various directive papers which do not so much help as hinder producers.

...I acknowledge that I looked forward with great interest to my meeting with Minister M. Busygin. What would he say about the state the sector has gotten into? What would he see as the ways to eliminate the long-standing lagging?

Mikhail Ivanovich immediately revealed his position. Yes, not everything is well in the pulp and paper industry, but talking about some hundreds of thousands of tons of underproduced paper--that is just the same as swatting a fly with a sledgehammer. It is necessary, said the minister, to construct new modern combines, then the problems will go away by themselves.

Later the conversation turned to other things--the profligate use of timber resources ("We are chopping down more than we are planting"), and the incorrect choice of priorities by planning organs in developing the sector.

Much of what M. Busygin said was convincing. And at the same time the clear preference which he gave to prospects of the distant future, avoiding urgent present problems, was disturbing. Building new combines is possibly a solution. But you can't look only at the horizon and ignore what is under your

nose. Making more complete and rational use of created capacities (and workers in the paper industry have an adequate amount of these)--that is the truly solicitous approach to the matter. But here in the sector, as we see, far from everything is smooth....

Let us speak frankly: the lagging of the paper and pulp industry has stretched out for a long time. Meanwhile, this obvious fact has not been assessed in a principled fashion in the headquarters of the sector.

Realizing that you have lost your way is taking the first step towards the correct road. Otherwise you will never get out of the woods....

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EFFECTIVE MEASURES FOR REDUCING COSTS OF BOILER-FURNACE FUEL

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 6,  
1985 pp 8-9

ZERKALOV, D. V., candidate of technical sciences

[Abstract] An analysis was conducted on the factors contributing to high fuel expenditures at boilers and furnaces in the hydrolytic and forest chemistry industry. Among the most prominent factors contributing to high fuel usage were loss of heat with waste gases, irregular heat distribution and inefficient heating of the boilers and furnaces due to poor design, scale and soot buildup, and incomplete combustion. Considerable fuel economies can be realized by correcting for the noted deficiencies, and by conversions to gas fuel whenever possible. A summary table is presented of the more important factors leading to poor fuel economy and the degree of inefficiency in fuel use that they engender.

[91-12172/12955]

UDC 676.164.085.2.06:665.947.2.004.14

MODIFIED TALL OIL FOR CABLE INDUSTRY

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 6,  
1985 pp 18-19

SHLYASHINSKIY, R. G., KLYUYEV, A. Yu., BOGOMOLOV, B. D. and PUYAT, S. S.

[Abstract] Technical steps are described for the treatment of tall oil with pentaerythritol for the production of rosin suitable for use in cables. The essential step includes treatment of the tall oil with 3.5 wt% pentaerythritol for 3 h at 200-260°C, with the resultant product designated as KMTK-1. In comparison with standard gum, rosin KMTK-1 differed only to a minor extent in dielectric properties and chemical composition, and was deemed suitable for use in cables as a less expensive substitute. Figures 2; references 2 (Russian).

[91-12172/12955]

MISCELLANEOUS

DATA BANK FOR SPECTRAL CHARACTERISTICS OF ORGANIC COMPOUNDS

Moscow NTR: PROBLEMY I RESHENIYA in Russian 2-15 Jul 85 p 7

YUDINA, L.

[Excerpt] There is a new sign on one of the buildings of the Novosibirsk Institute of Organic Chemistry of the USSR Academy of Sciences' Siberian Department. It reads: "Scientific Information Center for Molecular Spectroscopy". Here computers are taught how to solve complex problems of chemistry.

The center has created the country's largest machine data bank for spectral characteristics of organic compounds. Specialists can turn here for reference data, and they can get answers which a computer formulates on the basis of analysis of factual material that is stored in its memory.

One of the most important problems that the center is working on is finding the easiest and most convenient way for chemists to communicate with the machine in the language of structural formulas. Thanks to the development of an original semiautomatic device for coding and input of chemical information into the computer, it has become possible to quickly formulate different kinds of data banks of the type "structure-property".

"The development of hardware and software for communicating with the computer in the language of structural formulas," said Candidate of Chemical Sciences M. I. Podgornaya, deputy scientific director of the center, "has given impetus to work on machine planning of techniques of synthesizing complex organic compounds that have a given structure."

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